Review

Transition Metal Oxides and Their Composites for Photocatalytic Dye Degradation

Preety Ahuja ¹, Sanjeev Kumar Ujjain ^{1,*}, Rajni Kanojia ² and Pankaj Attri ³

¹ Research Initiative for Supra-Materials, Shinshu University, Nagano City 380-8553, Japan; drpreetyahuja@gmail.com

² Department of Chemistry, Shivaji College, University of Delhi, Delhi 110027, India; drrajnikanojia@gmail.com

³ Center of Plasma Nano-Interface Engineering, Kyushu University, Fukuoka 819-0395, Japan; chem.pankaj@gmail.com

* Correspondence: drsanjeevkujain@gmail.com

Abstract: Transition metal oxides (TMO) and their carbon composites have become a glittering upcoming material science candidate. Their interesting properties, such as their meticulous morphology, plentiful availability, flexible surface chemistry along with outstanding mechanical, thermal, and optical properties make them ideal for efficient photocatalytic dye degradation. An extensive range of TMO, and their carbon composites are reviewed highlighting the progression and opportunities for the photocatalytic degradation of dyes. Here, we concisely describe the numerous techniques to extend the optical absorption of these TMOs involving dye sensitization, metal doping, etc. Besides this, an overview of all aspects of dye degradation along with the prevailing challenges for future utilization and development of such nanocomposites towards highly efficient dye degradation system are also reported.

Citation: Ahuja, P.; Ujjain, S.K.; Kanojia, R.; Attri, P. Transition Metal Oxides and Their Composites for Photocatalytic Dye Degradation. *J. Compos. Sci.* **2021**, *5*, 82. <https://doi.org/10.3390/jcs5030082>

Academic Editor:
Francesco Tornabene

Received: 18 February 2021
Accepted: 12 March 2021
Published: 15 March 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: transition metal oxide; bimetallic transition metal oxide; carbon composite; photocatalytic; dye degradation

1. Introduction

With the increase in world population and rapid urbanization, natural resources are getting exhausted. Development of urban areas causes organic effluents from industries and agricultural activities, which not only cause threatens to human lives but also affected aquatic life very adversely [1]. Globally, 1.2 billion people are deficient in accessing safe drinking water, and millions die from uncontrolled spread of diseases and chronic illness transmitted via unsafe water [2,3]. Particularly, there is an explosive development in the dye and dyeing industries since last few decades. As effluents, many potentially hazardous compounds have been introduced into the environment, which are harmful for both flora and fauna on the planet. As per the World Bank's estimation, textile dyeing and treatment effluents results in 17 to 20% of water pollution [4]. The affecting factors broadly comprise of poor biodegradable waste such as used dyes and of which ~10–15% enter the environment through wastes. These dyes can be cationic, anionic or non-ionic depending on their chemical structure. The release of dyes in effluent results in perturbations of the marine life leading to severe effects on exposed organisms owing to the reduction in photosynthetic rate.

Moreover, water quality is significantly influenced due to the color of the dye, causing esthetic pollution, which is associated with contamination [5,6]. Willmott et al. has reported that dye concentrations as small as 0.005 mg dm^{−3} is perceptible in river water [7]. Today, 20% of our population has no access to safe water, 40% suffers owing to improper sanitary conditions and millions of people die every year from diseases communicated through unsafe water [2,8]. Dye effluent commonly contains chemicals which are toxic, carcinogenic or mutagenic to aquatic species [9,10]. In addition, human disorders say nausea, hemorrhage,

ulceration of the skin and mucous membranes [11] are caused due to the existence of dyes or their degradation products in water. Along with this, these dyes can also cause acute injury to the central nervous system and reproductive system [12]. This leads to deeper concern for colored wastewater discharges and convincing the dye users to espouse cleaner technology methodologies for benign dyeing strategies and upgrading dyes fatigue.

Consequently, significant efforts have been employed to initiate different suitable purification methods to destroy these pollutants. However, their incomplete removal during processing led to their presence in wastewater effluents in minute amount which is a matter of big concern towards the health and wealth of ecosystem, as they have endocrine disrupting potency [13].

Modernized society demands for pure water have made degradation of the dyes a great challenge that needs to be addressed for the well-being of humans and aquatic life. Several physical, biological and chemical techniques have been utilized for water purification (Figure 1). Adsorption and ion exchange are the most widely used physical methods for dyes removal resulting in high quality water [14]. However, the most commonly used adsorbents such as activated carbon have a high cost and hence replaced by other alternatives which demonstrate good efficiency [15,16]. Further, this method transfers pollutants to other phases that need to be treated. Another method involves coagulation/flocculation for color removal from textile effluents is associated with high-cost reagents, which impedes their practicability. Separation processes by utilizing membranes, reverse osmosis and ultrafiltration with microfiltration help detach the dyes from larger molecules in the wastewater. These processes have limited applications due to the inherent limitations, such as high expenditure, limited versatility, elevated salt content in the waste matter, replacement of membranes and problems associated with the disposal.

Figure 1. Different ways of dye degradation constitute the Physical, Chemical and Biological approaches.

Utilization of biological methods proved to be an economical alternative since it requires minimal major processing costs, but numerous dyes are deliberated to defy microbial attack. Different bacteria and fungi have been used to treat textile effluents via various biological processes [17–22]. Two conditions, aerobic and anaerobic, have been combined for the proficient removal of azo dyes from wastewater, as azo dyes are not efficiently metabolized under aerobic conditions. In contrast, biological enzymes under anaerobic

conditions utilize a high reduction rate of electrophilic azo-bond of the dye molecule to produce colorless aromatic amines [23]. Such amines are resilient to further anaerobic mineralization and are sometimes mutagenic to animals. Lourenco et al. suggested a sequential anaerobic–aerobic scheme utilized for wastewater treatment involving mineralization of the amines under aerobic environments via hydroxylation pathway with the ring-opening procedure [24]. Furthermore, the use of whole cells instead of enzymes has been given preference for the degradation of dyes in wastewater since cells can protect the enzymes from the severe environment. However, due to their complex structure with different chromophoric groups, dyes are enormously recalcitrant [23]. In addition, the frequent daily unpredictability of features of such wastewater enhances the difficulty of treatment [25]. Although several known physical and biological methodologies have been extensively utilized for decolorization [26], no one has materialized by way of complete remediation. Wastewater treatment via microbial biocatalysts offers potential advantages over different physical processes, but biological methods are rather inefficient, whereas physical methods are impeded in the operation scale.

Consequently, various chemical processing, such as chemical oxidation, solvent extraction, catalytic degradation, etc. for water purification, emerged. However, these are time consuming and high on cost hindering their practical utility. To provide a wholesome remediation, nanotechnology is the potential approach, focusing on unique attributes of materials emerging from nano dimensions that ensure the purification of water resources. This is possible through photocatalysis, a property exhibited by semiconducting oxides or more precisely transition metal oxides (TMO), whereby they absorb photons to undergo redox reactions, breaking complex organic molecules into simpler fragments [27]. The diffusion length of charged carriers (e^-/h^+) from bulk to surface is significantly reduced for nanoparticles facilitating these carriers' migration rate and hence enhancing the photoactivity. TMOs such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide (Fe_2O_3) and magnesium oxide (MgO) have been explored extensively in photocatalytic applications for water remediation [28,29]. Among them, the most widely utilized is TiO_2 owing to photochemical stability, chemical inertness, and ecologically benign [30]. In addition, its competitive rival, ZnO , has better electron mobility [31]. Even though they show excellent properties, their application in photocatalytic degradation (UV light driven) is hindered owing to wide band gap. Hence, band gap modification is required for improving the photodegradation efficiency, which will be more comprehensively discussed in later section.

Currently, nanotechnology-based water purification involves photocatalytic dye degradation mainly focusing on three major areas for efficient performance:

- i. Visible light-driven photocatalyst
- ii. High adsorption capacity
- iii. Large electron/hole recombination lifetimes

Due to the wideband gaps of the transition metal oxides, extensive research has been employed to redshift their band gaps towards visible light-driven photocatalysis. Besides, the higher bandgap, rapid electron/hole pair recombination further impedes the photocatalytic activity. This may arise due to low adsorption capacity of existing adsorbent, causing a significant bottleneck for dye mineralization [32,33].

In order to achieve the above-mentioned goals, two approaches are typically employed which are the doping of existing transition metal oxides with foreign transition metal ion to tune the band gap and hence, altering the optical absorption of the resulting nanocomposite. Introduction of foreign transition metal ions results in formation of spinel or mixed bimetallic transition metal oxides. Furthermore, co-adsorbents serve the purpose to enhance the adsorption capacity with larger electron/hole recombination lifetime. High adsorption capacity is achieved by the co-adsorbent, which will facilitate the charge transfer processes resulting in higher efficiency [32,33].

Besides, the large volume of literature assembled by the researchers, here we offer a concise insight of the research on efficient photo dye degradation via transition metal oxide-based composites, along with the latest drift towards photocatalytic studies.

2. Dye Degradation

Solids, in general, possess different band gaps which result in diverse properties. Based on varying bandwidths, they are classified as metals, insulators and semiconductors (Figure 2). Solids (like metals), have overlapped band gap regardless of the temperature. The higher band is the conduction band whereas the lower one is the valence band and possesses gap for semiconductors and insulators. Bandgap in insulators is very high, and hence it is difficult to excite electrons from the valence to conduction band, and the gap is called the forbidden gap. However, in semiconductors, the bandgap is small enough for the electrons to promote from valence to conduction band at room temperature. Their bandgap lies in the range of 0 to 7 eV bounding energy levels in the visible and UV light [34,35]. Photocatalysis involves light irradiation on the catalyst which functions as thermal energy and hence excites the electron from the valence to conduction band of the catalyst. Therefore, the band gap's width is the primary requisite for efficient photocatalyst, which strongly influences the electrical and optical characteristics of the material. To utilize the light from the solar spectrum, band gap engineering is the fundamental approach operated for semiconducting materials, and hence they are broadly utilized as photocatalysts.

Figure 2. Band gap structure for metals, semiconductors and insulators.

In the photocatalytic dye degradation, contaminants are destroyed utilizing transition metal oxides as efficient adsorbents, light source and oxidizing agent such as air/oxygen. Absorption of photons (with energy $\geq$ the band gap between valence and conduction band of transition metal oxide) results in electron transition from the valence band to the conduction band resulting in the formation of hole (h^+) in the valence band and electron (e^-) in the conduction band (Figure 3). Oxygen adsorbed on the photocatalyst is reduced by the electron in the conduction band, whereas the hole oxidizes the pollutant or sometimes it oxidizes water to produce $\bullet OH$ radicals. Here, h^+ and e^- act as oxidizing and reducing agents, respectively [32]. When reduction and oxidation do not proceed concurrently, electrons accumulate in the conduction band resulting in fast recombination of electrons and holes, reducing photonic efficiency. Hence, their consumption is a vital requirement to endorse photocatalytic performance. Various parameters such as light intensity, catalyst loading, pH, type of adsorbent, contaminant (dye) type and concentration etc. influences

photocatalytic dye degradation [33]. Among them, this article concentrates on adsorbent properties, favorable for photo dye degradation with high efficiency.

Figure 3. Different processes (reduction, oxidation, surface recombination, etc.) takes place after irradiation of photocatalyst.

3. Nanocomposites for Photocatalytic Dye Degradation

3.1. Transition Metal Oxides as Photocatalyst

Chemical reactions in the water system are greatly influenced by the light (visible and UV light). Most of the semiconductors can strongly interact with the photons' wavelengths as their band gaps lie in the same range. In addition to this, the large bandgap of these materials results in the absorption of UV light limiting their practical application because UV light only constitutes 5% of the solar spectrum. Besides suitable bandgap, potential adsorbents should be easy to produce, cost-effective, photostable and non-toxic for the environment [36,37]. The researchers have also explored numerous other techniques to extend the optical absorption of these transition metal oxides involving dye sensitization, metal doping, semiconductor coupling and non-metal deposition [38–44]. The purposes for utilizing these techniques are as follows:

- Enhance adsorption capacity at the catalyst surface
- Tuning the optical band gap or light absorption capability of the photocatalyst
- Preventing the recombination of charged carriers in combination with facilitated charge transfer

This section emphasizes the recent advances in various types of metal oxide nanoparticles and their composites for photocatalytic dye degradation from the wastewater.

3.1.1. Dye Degradation by Titanium Oxides

Photocatalytic reactions firstly reported by Fujishima and Honda et al. on the surface of TiO_2 (photocatalyst) which are photolysis of water, as shown below [45]:

Here, H_2 gas is produced from water and light interaction from solar spectrum (visible and UV), which can act as an alternative to fossil fuels [46,47]. It was then noted that the intermediate reactions resulted in formation of OH radicals, and hence, photocatalysis becomes important for the decomposition of water pollutants [48,49]. Researchers later focus on improving the efficiency of the involved photocatalysts (semiconducting oxides) for degradation of contaminants to purify water.

Earlier numerous studies have been reported for various photocatalyst, which produces photo excited e^-/h^+ pair for the decomposition of dyes. Among existing materials, TiO_2 proved to be the most active photocatalyst for dye degradation [38,50].

An outstanding review on metal doping for photocatalysis is reported by Carp et al. [37] with the main objective of reducing the band gap of the photocatalyst and the generation of intra-states between valence and conduction band resulting in UV to visible light absorption. The doped ion alters the recombination rate by acting as a trapping center for charge carrier and modifying the surface properties by enhancing adsorption capacity. Silver (Ag) nanoparticles loaded on different semiconductors have been illustrated as an effective approach for improving photocatalytic performance [51,52]. The metallic nanoparticle of Ag acts as a sink to accept the photoexcited electrons facilitating the reduction process and decelerating electron/hole recombination. Ag nanoparticles have also been utilized to tune metal oxide properties, i.e., TiO_2 , NiO and ZnO by surface plasmon resonance [42]. Excited by this, a number of research groups have explored the doping of TiO_2 by different transition metal ions [53–55]. Vanadium doped TiO_2 active under visible light illumination was reported by Klosek et al. After irradiation by visible light, excited vanadium donates an electron to TiO_2 conduction band promoting the oxidation of surface adsorbed molecules [56]. Boron-doped photocatalyst has also been explored and displays high performance in mineralization of Methyl orange (MO) with decolorization degree of 90% in 2 min [57]. Alternatively, non-metal doping results in redshift of the energy which is absorbed by the photocatalyst, resulting from bandgap narrowing in which valence band is elevated (Figure 4), with no modification in the conduction band [34,49,58].

Figure 4. Modification of band gaps on metal ion doping and for non-metal composite.

Doping of rare earth metal ions also enhances the potential of photocatalytic dye degradation owing to their distinctive chemical, physical and electronic properties. Associated f -orbital of the lanthanide ions has increased absorption of pollutants via Lewis base interaction and function as an efficient electron trapper. Du et al. suggested that doping TiO_2 with rare earth metal ion enhances its photocatalytic performance [59]. Ce doping

(1%) in TiO₂ was reported to display best decolorization performance of Methylene Blue (MB). Zhu et al. reported 91.2% decolorization efficiency for MB by Ce⁺³ doped TiO₂-SiO₂ after 180 min irradiation [60].

In addition, there also exist reports on simultaneous deposition and doping, Ag/Ag(I)-TiO₂ in which Ag(I) doping come up with the development of an isolated energy level of Ag 4d in TiO₂ bandgap [61]. Visible light illumination resulted in the absorption of visible light by isolated energy level of 4d. In contrast, the surface metallic Ag facilitates the photogenerated carriers (electrons and holes) separation resulting in higher visible light activity than the TiO₂ modified with Ag.

Another alternative to improve the visible light absorption or narrowing the bandgap is to substitute oxygen with inorganic ions (C⁺⁴, S⁻², etc.). Different methods have been used to produce visible light active TiO_{2-x}N_x photocatalyst along with the shift of absorption edge [62–67]. It is predicted to lower the bandgap energy because N2p states of dopant mix with the O2p resulting in the narrow bandgap. Moreover, TiO₂ oxygen sites replaced by nitrogen form isolated impurity energy levels above valence band, which will also narrow the bandgap. Strongly localized N2p states above the valence band (isolated empty states) incline to trap the photogenerated electrons, thus decreasing the photocurrent [68].

3.1.2. Dye Degradation by Zinc Oxides

In addition to TiO₂, Zinc oxide is a promising adsorbent for wastewater dye degradation owing to its low cost, non-toxicity and tunable morphological features. Daneshvar et al. reported a suitable alternative, ZnO₂ with similar photocatalysis mechanism as that of TiO₂ [69]. Notably, tunable morphology of ZnO also played crucial role in wastewater remediation. The ZnO hierarchical mesoporous microspheres displayed remarkably high adsorption capacity (334 mg g⁻¹) for Congo red dye in comparison with the commercially available ZnO powder [70]. Hollow microsphere of ZnO-ZIF-8 [Zn(MeIM₂)] has also been explored for dye adsorption and reported with further enhanced efficiency by the core-shell structure of the resulting composite [71]. Recently, green synthesis of ZnO has attracted extensive attention as a feasible, highly efficient and eco-friendly protocol to eliminate the environmental impact of commonly utilized synthesis methods in laboratory. The Panos extract mediated quaker ladies type ZnO nano flower (ZnO/QNF) degraded the 15 mg L⁻¹ MB, Eosin Y (EY) and Malachite green (MG) to >99% within 80, 90 and 110 min, respectively [72]. ZnO nanoparticles synthesized using the Calliandra hematoccephala leaf extract shows 88% MB degradation, under solar radiation in 270 min [73], while ZnO nanoparticles obtained using Quince seed Mucilage as stabilizing agent displays 80% degradation of MB within 2 h [74]. Furthermore, ZnO nanoparticles synthesized via extracellular culture filtrates of *Aspergillus niger* degraded the Bismarck brown dye with 90% efficiency [75]. Additionally, Cr-doped ZnO with different amount of Cr³⁺ were reported for the removing anionic dyes by enhancing the surface defects on ZnO nanoparticles. This correspondingly resulted in formation of hydroxyl groups for the protonation leading to positive charge generation. This positively charged ZnO nanoparticles undergo strong electrostatic interaction and selectively eliminate the anionic dyes driven by photocatalysis [76].

3.1.3. Dye Degradation by Iron Oxides

Extensive availability of iron oxide is further reported with large photocatalytic activity. Advantageously, their recovery from the system owing to the inherent magnetic effect endow a promising adsorbent alternative. Photocatalytic degradation features of iron oxides (Fe⁺³) in different forms such as α -Fe₂O₃, γ -Fe₂O₃, α -FeOOH, β -FeOOH, and γ -FeOOH were explored for the visible range dye degradation. Further, azo dyes are demineralized by iron oxide powder, resulting in substituted benzene and naphthalene as degraded products [77]. Optimized crystallite size (35, 100, 150 nm) of the iron oxide nanoparticles were also demonstrated to successfully degrade Congo red. Notably, the Congo red was degraded in presence and absence of visible light using the 35 nm nanopar-

ticles with no distinct effect on the photocatalytic decomposition [78]. The addition of Zn^{2+} and Al^{3+} to the hydrothermal reaction system resulted in the formation of iron oxides with cubic and disc structures, respectively, which successfully degraded Rhodamine B (RB) in the presence of 30% H_2O_2 solution. The photodegradation processes amplified significantly with increasing amount of H_2O_2 which facilitate diffusion onto the iron oxide surface enhancing the generation of reactive $\bullet\text{OH}$ [79]. Additionally, Shenoy et al. studied the effect of morphology-dependent surface charges of iron oxide for the visible light photocatalytic degradation of MB. The nanorods morphology with high negative surface charges (-20.8 mV) showed $\sim 86\%$ MB degradation, which outperformed other morphologies like hexagonal, oval and agglomerated nanoparticles [80]. Furthermore, iron oxide nanoparticles synthesized via various green routes also demonstrated high degradation efficiency. Teucrium polium leaf extract synthesized iron oxide nanoparticles (IONPs) degraded the MO dye with 73.6% efficiency in a 6 h reaction [81], while, magnetic $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles synthesized using Cynometra ramiflora fruit extract demonstrated 94% degradation of MB in 110 min, under sunlight irradiation [82]. Iron oxide nanoparticles synthesized using pomegranate (*Punica granatum*) seeds extract also possesses 95% reactive blue dye degradation under UV light irradiation for 56 min [83]. However, rod-like Fe_2O_3 magnetic nanoparticles synthesized using the Peltophorum pterocarpum leaf extract could achieve 92% MB degradation in minimum 27 min. This rapid degradation has been related to the “electron relay process” in which BH_4^- ions generated from NaBH_4 transfer electrons to Fe_2O_3 nanoparticles generating a negatively charged environment to degrade the MB dye to harmless products [84]. Such green synthesized nanoparticles can potentially serve as an efficient catalyst for environmental remediation. Different metal doping in iron oxide alters the recombination process of charge carriers and augments the photocatalytic activity. Different Au loadings in $\text{Au-Fe}_2\text{O}_3$ aerogels were utilized as photocatalysts for mineralization of Disperse Blue 79 dye. This correspondingly promoted the accumulation of the photogenerated electrons and delayed charge carrier recombination, improving the efficiency [85].

3.1.4. Dye Degradation by Other Oxides

Various photocatalysts like CdS, GaAs and PbS are not stable since they undergo photocorrosion besides their toxicity [36,86]. Additionally, the low charge separation efficiency of photoexcited carriers in TiO_2 impeded its applicability [87]. So, several other TMOs involving MnO_2 , CuO_2 , Ag_2O modified MoS_2 etc. are explored as photocatalyst. MnO_2 nanosheets modified with fiber glass was developed by Zhang et al. [88] and explored for mineralization of MB at different pH with efficiency $> 95\%$. Pandit et al. reported colloidal MnO_2 catalyzed degradation of methyl red and MO dye with high efficiency [89]. Besides colloidal form, mesoporous MnO_2 also exhibits superb performance for MB mineralization in H_2O_2 at neutral pH and it can be recycled with tiny decrement of catalytic activity at room temperature [90].

Dyes are also used as sensitizers in the visible region including erythrosine B, thionine, rhodamine and ruthenium trisbipyridine [91–94]. Dye sensitization process involves indirect electron injection from the excited dye rather than the photocatalyst. Firstly, dye gets excited to singlet and triplet states followed by conversion to dye radicals. Electrons are then injected to the photocatalyst conduction band and interact with the adsorbed oxygen [95]. In addition to this, photocatalytic activity can be enhanced by coupling two semiconductors with different bandgaps providing more efficient separation of charged carriers and extended light absorption range [96–98]. Ternary nanocomposite $\text{Cu}_2\text{O-BiVO}_4\text{-WO}_3$ has also been explored and showed augmented photocatalytic activity compared to their pristine components due to better charge separation [99].

Ag_2O nanorods modified MoS_2 microflowers ($\text{Ag}_2\text{O/MoS}_2$) based heterostructures exhibited ten times larger photocatalytic efficiency. This is ascribed to consequent morphology and enhanced charge separation efficiency resulting from synergistic effects [100].

Effect of different oxidants like peroxymonosulphate (PMS), peroxydisulphate (PDS) and hydrogen peroxide (H_2O_2) on photocatalysis had been further explored by utilizing different adsorbents [38]. Peroxydisulphate (PDS) showed the off-putting effect on MB demineralization, whereas H_2O_2 and peroxymonosulphate (PMS) enhances the degradation rate.

3.2. Bimetallic Transition Metal Oxides as Photocatalyst

Visible light-driven photocatalyst are the ideal alternative as solar energy constitutes 43% of the visible light. Monometallic oxides, their reduced counterparts or noble metal doped derivatives have been utilized in MB degradation under visible light, however, their efficiency is impeded by light absorption characteristics [101–104]. This can be made in our favor by tailoring the band gap of the resulting composite, which will alter the composite's light absorption feature. Hence, bandgap engineering is a vital requirement for high efficiency of the adsorbent in photo dye degradation. Doping with other transition metal oxide is a typical approach resulting in energy states' generation between valence and conduction band for electronic transitions due to photoexcitation [105]. Mahmood et al. reported that optimum doping of Mn^{+2} in ZnO enhances its photocatalytic activity by narrowing its bandgap [106]. Further, Deka et al. reported the tuning of bandgap of ZnO with Mn content ($\text{Zn}_{1-x}\text{Mn}_x\text{O}$ with $x = 0.02, 0.05$) which resulted in varying performance [107]. The photocatalyst's effective performance also depends on various other parameters say pH, dye concentration, light intensity etc. which have been explored by investigating the influence of these factors on the rate of photoactive dye degradation utilizing CeCr_2O_5 as photocatalyst [108]. With the increase in dye concentration, the photocatalytic rate first increases and then decreases. This phenomenon arises because more dye molecules are available for degradation with the increase in dye concentration, consequently enhancing the rate. After a certain dye concentration, rate declines. This is attributed to the dye's filtering action where it acts as filter for incident light, inhibiting the desired light intensity to approach the semiconductor surface.

CeO_2 acts as a promoter for $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ has been explored by Liu et al. [109] for photocatalytic azo dye degradation. They concluded that doping of CeO_2 results in efficient dispersion and smaller particle size of Fe_2O_3 presenting more active sites. Further, CeO_2 presence increases the chemisorption of oxygen, thereby improving the redox properties of the photocatalyst. CeO_2 is also doped in ZnO by Saravanan et al., and the resulting composite is found to exhibit improved photodegradation rate as compared to ZnO [110]. CeO_2 nanoparticles, owing to their lower bandgap, show enhanced photoactivity of the composite on visible light irradiation. This enhancement on visible illumination is attributed to CeO_2 nanoparticles, which capture the electrons with hydroxyl radical formation from the holes and, hence, prevent the electron/hole recombination. In addition, the composite shows efficient dispersion of ceria crystallites on ZnO [111,112] with higher surface area, presenting more and more active sites for the redox reactions. Magesh et al. [113] found that redshift is observed for TiO_2 modified with Ce compared to TiO_2 in UV-vis spectrophotometry and optimal Ce loading at 0.5–2.0% in the mixed oxide $\text{CeO}_2\text{--TiO}_2$ proved active under visible light for the MB photocatalytic decomposition. Photocatalytic activity of CuO/CeO_2 was also explored and reported to exhibit high performance owing to redox behavior of CeO_2 and its strong interaction between CuO and CeO_2 [114]. Irradiation by different light on the photocatalyst tailors the photodriven catalytic performance. Tung et al. have reported that under UV light irradiation, iron-doped TiO_2 reveal consideration increment in photoactivity than that of pure TiO_2 or Iron oxide [115]. This enhancement may be ascribed to impedance of electron/hole recombination with the incorporation of Fe ion in TiO_2 lattice. On the other hand, photoactive performance of the catalyst transforms under visible light state. It illustrates that pure iron (II, III) oxide exhibits excellent photoactive behavior which surpasses that of TiO_2 . Iron doping at 0.5 mol in TiO_2 made it comparable and for 1 mol, no increment was observed. Hence, iron-doped TiO_2 (photocatalyst) reacted differently under UV and visible light with no adverse effect on photoactivity in the former

case. The formation of recombination sites was observed via iron doping in TiO_2 under visible light, thereby reducing photodriven catalysis. Zhu et al. also supported the above finding suggesting that the rate of recombination was decreased by utilizing iron ions as hole or electron snare in TiO_2 [116]. Photocatalytic studies of $\text{MnO}_2/\text{Fe}_3\text{O}_4$ nanocomposite show high photocatalytic efficiency and high stability with recyclability towards the degradation of MB under UV-vis illumination [117].

Different strategies have been reported to enhance the photocatalytic efficiency or retard the electron/hole recombination rate in mixed oxides. TiO_2 -NiO mixed oxide developed by sol gel method reportedly have high efficiency for photodriven MO removal [118]. This enhancement is attributed to the induced n-p junction at the interface, which prevents electron/hole recombination upon irradiation by light. This can be explained by (Figure 5) considering the existence of both TiO_2 (n-type, electron rich) and NiO (p-type, hole rich) phases or n-p junction at the interfacial contact where diffusion of electrons and holes takes place to p-type and n-type semiconductors, respectively. At equilibrium, the internal electric field arises due to accumulation of electrons and holes, which act as potential barrier and prevent electron/hole recombination. They also investigated the variation of nickel content on catalytic efficiency of the synthesized composite. Highest efficiency was exhibited by $\text{Ti}_{75}\text{-Ni}_{25}$ composite, and with further increment in Ni content, specific surface area and total pore volume of the resulting composite diminishes, which is detrimental for photocatalytic reactions.

Figure 5. Schematic showing p-n junction at the interface of p-type NiO and n-type TiO_2 semiconductors for improved photocatalytic degradation of MO.

Sreethawong et al. loaded noble metal on the mixed oxides to enhance their photocatalytic rate [119]. Mesoporous assembled TiO_2 - SiO_2 mixed oxides loaded with monometallic Pt and bimetallic Pt-Au were studied as adsorbents under visible light driven catalysis for different loadings of Au and Pt. Similarly, Fe was introduced to ZnO/SiO_2 to improve their catalytic performance by shifting the absorption bandgap threshold from UV towards visible region, thereby modifying surface physical and chemical properties [120]. Various other factors say dye solution pH, initial dye concentration, illumination time, and catalyst loading effecting photo-mediated oxidation of MB were investigated and explored for the photocatalytic process's optimal conditions. The efficiency of photocatalysis decreases with increase in pH with a value of $\sim 99.9\%$ when pH increases from 2 to 4. However,

for negatively charged MB in acidic medium and positively charged ZnO below pH 9, increase in pH change the charge on ZnO by absorbing OH^- ions favoring the formation of $\bullet\text{OH}$ radicals resulting in diminished photoactive efficiency. This is due to gradual increase in electrostatic repulsion between anionic dye and ZnO. Additionally, catalyst loading also has considerable effect on photoactivity of Fe/ZnO-SiO₂. When loading increased above 0.1 g, efficiency decreases owing to agglomeration of catalyst particles as a consequence of increase in particle size and decrease in surface area, diminishing the number of surface-active sites. Further, the effect of different loading of MnO₂ over TiO₂ is explored by Xue et al. and reported to have high surface area and large pore size with enhanced adsorption properties over whole region of visible light [121]. The enlargement of the pore size is explored and attributed to the coating mechanism where dopant Mn^{+2} is coated onto the host in the synthesis procedure. During the synthesis, the formation of TiO₂ nanoclusters takes place with the oxidation of Mn^{+2} to MnO₂ in air which resist TiO₂ nanoclusters to join together. The clusters were thus prevented to come close to form a small pore, subsequently affected the crystallization of TiO₂. This led to remarkable absorption of visible light due to narrow band gap of MnO₂. Wang et al. reported a SnO₂-TiO₂ photocatalyst based on TiO₂ nanofibers by electrospinning followed by hydrothermal treatment [122]. Under UV light illumination, SnO₂-TiO₂ composite exhibits almost 2.5 times higher than TiO₂ photoactivity for RB mineralization. Li et al. synthesized MnO₂ loaded CuO nanosheets and reported to possess high catalytic activity due to its composite phases, large surface area and dispersibility [123]. Series of CuO/MnO₂ compounds with different CuO loadings was synthesized and demonstrate the highly efficient CuO/MnO₂ interfaces as active sites for photocatalysis [124]. MnO₂ layer is also coated on CuO to form nanorod array which addresses the issues related with the powder catalysis say easy agglomeration, difficult separation and possible secondary pollution [125]. In spite of this, metal vanadates are also widely utilized for photocatalysis. Recently, bismuth vanadate, BiVO₄ with layered structure and bandgap 2.4 eV was reported with varying molar ratio of Bi to V [126]. By alteration in the molar ratio, different crystal structures were obtained, tetragonal scheelite (ts), monoclinic scheelite (ms) and tetragonal zircon (tz). Amongst them, a higher photocatalytic activity under UV light has been exhibited by ms-BiVO₄, despite the consequences of its morphology with different dyes say RB and MB. Moreover, it demonstrates the potential of ms-BiVO₄ under 6h visible light illumination with degradation efficiency of 65.0% for MB and ~77.8% for RB. Shang et al. [127] also reported nanosized BiVO₄ (dia 60 nm) with visible light-driven photocatalytic activity. They suggested that nano BiVO₄ possessed excellent photocatalytic efficiency towards the degradation of RB in 40 min. Furthermore, Yin et al. [128] synthesized ms-BiVO₄ by using cetyltrimethylammonium bromide (CTAB) and reported that CTAB transformed the mechanism of reaction with the formation of an intermediate BiOBr. Besides high photocatalytic efficiency, no considerable loss was witnessed after five cycles, signifying the high stability and absence of photocorrosion during RB degradation by ms-BiVO₄.

Despite metal vanadates, different metal molybdenum oxides were reported as efficient photocatalysts for the treatment of wastewater using UV or visible light illumination [129–131]. Xu et al. demonstrated high photocatalytic degradation activity of 90% under visible light irradiation for MO treatment using zeolite supported Bi₂MoO₆ [131]. This enhanced performance is attributed to uniform distribution of Bi₂MoO₆ nanoparticles on zeolite. ZrMo₂O₈ was reported by solid state technique and possess ZrO₈ and Mo₂O₈ polyhedra [132]. It has specific degradation properties towards cationic dyes, say malachite green (MG) and RB.

Various other bimetallic oxides such as NaTaO₃, CoTaO₆ and CeTaO₄ were supposed to have extended conduction and valence band, increasing the lifetime of photogenerated transporters, promoting the redox reaction on the catalyst surface [133–136]. Application of Fe-Co mixed oxide with varying Fe/Co ratio for degradation of 2, 4-dichlorophenol was explored and proved effective than bulk Co₃O₄ [137]. Authors also examined Co_xFe_{3-x}O₄ nanoparticles for RB heterogeneous degradation and revealed that higher cobalt content

results inefficient removal of the dye. Another bimetallic oxide NaBiO_3 examined under visible light irradiation for RB degradation via direct cleavage of the conjugated chromophore of dye molecule along with the degradation as dominating mechanism [138].

Besides this positive effect of bimetallic oxide interaction, the photocatalytic efficiency can also be poisoned via metal-metal ion interaction. Influence of different crystallographic forms of MnO_2 on Degussa P-25 TiO_2 resulted in photocatalytic inhibition or complete deactivation depending upon the amount of MnO_2 [139]. This is due to the heterojunction formation at MnO_2 - TiO_2 interface which alter the chemical state of Ti^{+4} and O^{-2} sites in TiO_2 . MnO_2 also widens the bandgap of TiO_2 , thereby diminishing the UV absorption by creating impurity energy levels which serve as a recombination center for photoexcited charged carriers.

Among various mixed oxides formed via doping of foreign transition metal ion in host transition metal oxides, spinel oxides form a special class which have narrower bandgap with efficient catalytic properties. Spinel oxides synthesized by different methods possess high electrochemical activity with facilitated charge transfer [140–145]. Nano iron-cobalt spinel oxide was explored for photocatalytic activity via mineralization of monoazo-dye Acid Orange 7 with sulfate radicals in aqueous solution [146]. Quenching studies established that sulfate radicals are the primary species produced in the dye's catalytic degradation, which enhances the efficiency of the photocatalyst. Further, 3D magnetic $\text{ZnFe}_2\text{O}_4/\text{MnO}_2$ hybrid was explored for photocatalysis and found to possess better activity (owing to its high BET surface area) with easy recyclability from reaction solution [147]. Cobalt ferrite, CoFe_2O_4 was synthesized by co-precipitation on the TiO_2 surface to achieve recyclability with efficient photocatalytic ability which is estimated by following the degradation kinetics of textile dye in absence and presence of different electron acceptors [148]. It displayed maximum increase in the decomposition of Reactive red 120 (dye) in peroxomonosulphate (PMS) as compared to other electron acceptors. Ordinary NiCo_2O_4 and their core ring structured nanoplatelets were developed by Cui et al., which reports that the core ring NiCo_2O_4 nanoplatelets display elevated photocatalytic activity MB demineralization under visible light [149]. This enhanced property is attributed to smaller size, high absorption capacity with active and efficient internal electronic transitions. In addition, the core ring structure provides larger surface area and active surface Co atoms which could be the primary reason for outstanding photoactivity. Various other composites of doped transition metal oxides or bimetallic oxides with improved photocatalytic activity are included in Table 1 [132,150–161].

3.3. Carbon Based Composites as Photocatalyst

Another approach is to enhance the adsorption capacity with larger electron/hole recombination lifetime. This can be achieved by supporting the transition metal oxides over co-adsorbent (support) which should have high adsorption capacity. The co-adsorbent should have high surface area and network conductivity for efficient adsorption and facilitated charge transfer processes, respectively. Carbonaceous materials such as activated carbons, carbon nanotubes and graphene are interesting and potential material for co-adsorbents owing to their higher surface area, unique pore structure and high conductivity [162–168]. Predominantly, the functions of co-adsorbent or support are as follows:

- i. Reduce agglomeration of the particles
- ii. Enhance surface area of the resulting composite
- iii. Govern the life span of the photocatalyst via reducing the recombination rate of charged carriers

Activated carbon- TiO_2 composites have been reported to exhibit improvement in photocatalytic activity attributed to the high adsorption capacity of the support and ready passage of charged carriers to TiO_2 particles [169–173]. However, under-exploitation of nanotexture and nanoscale phenomena with untackled bandgap engineering needs researchers to explore other alternatives [174,175]. Carbon nanotubes (CNTs) are reported to possess effective synergism with TiO_2 to enhance photocatalysis by diminishing the electron/hole

recombination [176–178]. Hoffmann et al. reported TiO₂–CNT composite with transference of photogenerated electrons to CNTs and holes to TiO₂, thus impeding the recombination of electrons and holes [179]. MWCNT TiO₂ composites have been extensively reported to improve their photocatalytic activity [180,181]. Magnetic photocatalyst, NiFe₂O₄/MWNT was synthesized by hydrothermal method and exhibited high photoactivity [182]. The poorly active NiFe₂O₄ nanocrystals are significantly converted into active one in the presence of MWNT, and this is attributed to synergism between the two with effective charge transfer and declined rate of recombination of photogenerated carriers. In addition to this, their remarkable magnetic property made it efficiently recyclable using an external magnet.

Table 1. Photocatalytic performance of bimetallic transition metal oxides. N.A. = data not available.

Photocatalyst	Synthetic Method	Performance	Reusability	Reference
ZnO microflower on Stainless steel (SS)	Spray pyrolysis of zinc acetate on SS	Decolorization efficiency (DE) 96% in 120 min under Sunlight	98% efficiency after 4 cycles	[150]
Mn–ZnO	Grinding Zn(NO ₃) ₂ ·6H ₂ O and Mn(CH ₃ COO) ₂ ·4H ₂ O using NaOH oxidant and SDS capping	DE 99% in 20 min under visible light	96% efficiency after 4 cycles	[151]
WO ₃ /SiO ₂	Impregnation followed by calcination Sodium Tungstate Dihydrate on SiO ₂ monoliths	DE 96% in 120 min under visible light	80% efficiency after 5 cycles	[152]
ZnO–TiO ₂	Sol gel synthesis using TiCl ₄ and Zn(CH ₃ COO) ₂ with calcinations at (160–900°C)	DE 100% in 10 min under UV irradiation	N.A.	[153]
WO _x –TiO ₂	Sol gel synthesis with thermal activation in vacuum	DE 100% under visible irradiation in 240 min of irradiation time	90% efficiency after 5 cycles	[154]
Fe, Co, Ni, Cu, Zn –TiO ₂	Sol gel method modified with ionic liquid	DE 90% Fe–TiO ₂ 80% Co–TiO ₂ 12% Ni–TiO ₂ 8% Zn–TiO ₂ 20% Cu–TiO ₂ Under UV irradiation of 120 min	N.A.	[155]
ZnO–SnO	ZnO by impregnation on silica	DE 90% under UV irradiation for 60 min	N.A.	[156]
Mn ⁺² –ZnO	Co-precipitation of zinc acetate with manganese acetate dopant	DE ~93.3% under UV illumination for 120 min	N.A.	[157]
BiVO ₄	Hydrothermal synthesis from Bi(NO ₃) ₃ ·5H ₂ O + NH ₄ VO ₃	DE 100% msBiVO ₄ 92.9% tz-BiVO ₄ 30.5% ts-BiVO ₄	N.A.	[126]
Bi ₂ WO ₆	Hydrothermal method	DE 97% under visible light irradiation of 320 min	N.A.	[158]
ZnWO ₄	Template method involving H ₂ WO ₄ and Na ₂ WO ₄	DE >95% under UV irradiation of 40 min	N.A.	[159]
ZnWO ₃	Impregnation method	~90% under laser irradiation for 15 min	N.A.	[160]
β- ZrMo ₂ O ₈	Solid state synthesis	No data	N.A.	[132]
CeO ₂ –TiO ₂	Polymer assisted method	24% visible irradiation of 90 min	N.A.	[113]
β-SnWO ₄	Solid state reaction	90% under visible irradiation of 120 min	N.A.	[161]

Among various carbonaceous material, graphene, two-dimensional sheets of sp² hybridized carbon, possess high charge carrier mobility with excellent mechanical strength [183]. Graphene can tailor the particle size and microstructure of the guest material and pro-

mote electron transfer in photocatalytic reactions [184]. Direct growth of transition metal salt on graphene oxide (GO) has been widely used for graphene/metal oxide composites [185]. In spite of this, various other graphene-based composites are in-situ synthesis and hydrothermal or solvothermal approach.

3.3.1. In-Situ Synthesis

During this, metal salts and graphene oxide (GO) are used as substrates. The salt is then added to GO (dispersed solution) followed by conversion to metal oxide in the oxidizing agent's presence, followed by the reduction of GO to graphene [141–143,167]. Graphene–ZnO composite was synthesized by adsorbing Zn^{+2} ions on graphene oxide sheets in the presence of NaOH and NaBF_4 followed by drying at $150\text{ }^\circ\text{C}$ [186]. Similarly, SnO_2 and TiO_2 were grown over graphene by taking SnCl_2 and TiCl_3 as substrates [187]. Different morphological structures were obtained by reducing Sn and Ti salts in presence of GO by the same method. This can be attributed to different hydrolysis rate of the salt with their reduction abilities. Researchers have utilized different methods for dispersing graphene oxide while synthesizing different graphene-based composites via in-situ method [188,189]. Anionic surfactants have also been used for stabilizing graphene in aqueous solution for in situ growth of TiO_2 over graphene [190]. Whereas, Park et al. reported graphite TiO_2 composite via exfoliation–reorganization of graphite oxide without using any chemical reagents in aqueous slurry [191].

3.3.2. Hydrothermal Approach

During hydrothermal growth, precursors (semiconductor oxide) are loaded on graphene oxide in a dispersed medium followed by a higher temperature reduction. ZnFe_2O_4 /graphene composite was synthesized by the same method with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors [192]. During growth, metal salts are oxidized with a reduction of graphene oxide. In-situ hydrothermal growth was utilized for graphene– BiWO_6 by Mukherji et al. in the presence of graphene oxide [193]. Shen et al. synthesized graphene TiO_2 composite via hydrothermal growth with scalable methods by utilizing water and glucose (reducing agent) [194]. Graphene TiO_2 composite was dispersed by controlling the hydrolysis via one-step solvothermal approach to achieve a uniformly dispersed metal oxide over graphene [37].

3.3.3. Photocatalytic Activity

Graphene TiO_2 nanocomposite, obtained via chemical oxidation of graphene suggested “on demand” graphene–metal oxide mechanism [195]. Functionalized GO nanosheets have efficient binding sites for metal oxide particles (TiO_2 , ZnO_2) and remain in solution without aggregation [196]. After photo-irradiation, the electrons interact with GO nanosheets to remove various oxygen functionalities yielding reduced graphene oxide (RGO) [197,198]. Some electrons are used for reduction purpose, and others are stored in RGO. The graphene TiO_2 can be recovered after solvent evaporation. Photocatalytic degradation of MB using TiO_2 nanorods GO composite exhibits anticharge recombination mechanism [199]. Authors found that the electrons at GO react with adsorbed oxygen to form $\bullet\text{OH}$ radicals reducing the recombination of charge carriers (e^-/h^+). Further, graphene presence in the composite influences the morphology and particle size distribution in the composite and accordingly alters the photocatalytic performance. Zhou et al. showed the uniform dispersion of TiO_2 nanoparticles on graphene sheets with narrow particle size distribution resulting in superior photocatalytic activity under simulated sunlight irradiation [200]. The electron/hole pairs are produced in TiO_2 upon illumination with UV light and the photoexcited electrons transfer to graphene sheets, scavenged by dissolved oxygen and promote the electron/hole separation. Additionally, Du et al. demonstrated the improved photocatalysis by ordered macro-mesoporous TiO_2 –graphene composite towards decomposition of MB in water than bare mesoporous TiO_2 film [188]. All the

above results of graphene-based composites displayed that graphene can promote charge separation in the composites and consequently results in high photocatalytic activity.

Graphene–ZnO composite was reported by adsorbing Zn^{+2} ions on GO sheets followed by addition of NaOH and NaBH_4 [186]. Various graphene composites (ZnO–graphene, Co_3O_4 –graphene, Mn_3O_4 –graphene, etc.) have been explored for their photocatalytic application to purify wastewater [186,201,202]. These composites showed high adsorption capacity and large charge separation facilitating overall performance. The significant role of graphene in the graphene TiO_2 composite is demonstrated by Zhang et al. [203] during the degradation of MB in water (Figure 6). Role of graphene and CNT were further explored by making their nanocomposites $\text{CuO}.\text{ZnO}.\text{Fe}_2\text{O}_3/\text{rGO}$ and $\text{CuO}.\text{ZnO}.\text{Fe}_2\text{O}_3/\text{CNTs}$ by utilizing against MB dye [204]. The resulting nanocomposites engendered stress in their lattice, resulting in some defects. These consequently resulted in enhanced chemical reactivity with improved efficiency owing to the newly generated electronic state resulting from varied interactions such as metal–metal, metal–oxygen–metal.

Figure 6. (a) Schematic of P25-GR and probable process of photodriven degradation of the dye (MB) over P-25-GR with TEM micrograph (b) of the composite. Comparison of photocatalytic activity in the degradation of MB under (c) UV light ($\lambda = 365$ nm) and (d) visible light ($\lambda = 400$ nm). Adapted with permission from Ref. [203]. Copyright 2010, American Chemical Society.

In addition, the graphene content in the composites significantly influences the photocatalytic efficiency. The effect of composites with different graphene content has been studied via photocatalytic degradation of MB in water [205]. Bai et al. utilized $\text{Zn}_{1-x}/\text{graphene}$ composite and provide insights for the development of graphene-based defect type material [206]. Superior photocatalytic activity of the synthesized composite corresponds to synergic effect of graphene and Zn_{1-x} surface defect layer. The electron/hole separation results due to the elevation of highest occupied molecular orbital (HOMO) of graphene and $\text{O}i''$ ZnO_{1-x} defect level in $\text{Zn}_{1-x}/\text{graphene}$ composite (Figure 7). Non-stoichiometric $\text{W}_{18}\text{O}_{49}$ has been reported as a potential visible-driven photocatalyst due to its unusual defective structure [207].

Figure 7. Schematic demonstrating the photocatalytic process over ZnO_{1-x}/graphene. Photocatalytic degradation of MB over ZnO_{1-x} and ZnO_{1-x}/graphene under illumination of (a) visible light and (b) UV light. Adapted with permission from [206]. Copyright 2013, American Chemical Society.

Du et al. further developed an approach to improve the charge carriers' diffusivity by employing hierarchical porous systems [188]. Macro-mesoporous titania graphene composite reduces the mesopore channel's diffusion length and enhances the effective surface area, resulting in diminished charge recombination rate. High photocatalytic efficiency of MnO₂ graphene composite is attributed to synergism between graphene and MnO₂ via efficient electron transfer channels with the high surface area for photoactive mineralization of MB [208]. Here, the adsorption–oxidation–desorption mechanism is involved for MB degradation. Firstly, MnO₂ are adsorbed on graphene surface via π - π conjugation, which effectively increases the MB concentration near the surface, enhancing the catalytic rate. Therefore, the coupling between adsorption and catalytic reaction for MnO₂/RGO composite results in efficient decomposition of MB compared with bare components. ZrO₂-graphene composites are also analyzed for photocatalysis and observed that degradation time decreases with enhanced degradation factor due to the inclusion of graphene in ZrO₂ [209]. This is attributed to the immediate shifting of electrons to graphene followed by the generation of electrons and holes on irradiation. The conjugated (sp²) carbon lattice increases light absorption range thereby promoting charge separation. In allusion to this, various other composites of graphene and transition metal oxides resulted with improved photocatalytic activity are presented in Table 2 [210–220].

Table 2. Photocatalytic properties of graphene-based composites (photocatalysts).

Composite Photocatalyst	Mass Fraction of Graphene	Photocatalytic Activity	Reusability	References
P25-G	5 wt % 10 wt % 20 wt % 30 wt %	R_{H_2} 26 $\mu\text{mol h}^{-1}$ 60 $\mu\text{mol h}^{-1}$ 74 $\mu\text{mol h}^{-1}$ 37 $\mu\text{mol h}^{-1}$	N.A.	[183]
TiO ₂ -G	6.5 wt %	80 μmol in 5 h	N.A.	[184]
TiO ₂ -G SnO ₂ -G	15 wt % 15 wt %	Reaction rate 0.0057 min^{-1} 0.011 min^{-1}	N.A.	[187]
TiO ₂ -G	0.6 wt %	Reaction rate 0.071 min^{-1}	N.A.	[188]
TiO ₂ -GO	1 wt %	175 mmol in 3 h	N.A.	[191]
ZnFe ₂ O ₄ -G	20 wt %	DP 99%	95% efficiency after 10 cycles	[192]
TiO ₂ -G	25 wt %	R_{H_2} 4 $\mu\text{mol h}^{-1}$	N.A.	[194]
TiO ₂ -G	10 mg 30 mg 50 mg	DP 58% DP 75% DP 72%	N.A.	[209]
TiO ₂ -G Mixed phases	5wt% GO	Degradation Percentage (DP) 93%	90% efficiency after 5 cycles	[210]
TiO ₂ -GO	20wt %	DP 96.62%	80% efficiency after 3 cycles	[211]
TiO ₂ /ZnO/G	5wt% GO	DP 99.2%	>92% efficiency after 5 cycles	[212]
Fe ₂ O ₃ /TiO ₂ -G	20 mg	DP 100%	>90% efficiency after 4 cycles	[213]
TiO ₂ -GO	0.13 wt % 0.14 wt % 0.25 wt % 0.51 wt %	DP 26 % DP 35 % DP 22 % DP 18 %	N.A.	[214]
ZnO-G	0.05 wt % 0.5 wt % 1.0 wt % 2.0 wt % 3.0 wt % 5.0 wt %	Reaction rate 0.047 min^{-1} 0.056 min^{-1} 0.069 min^{-1} 0.098 min^{-1} 0.091 min^{-1} 0.072 min^{-1}	No change in photocatalytic activity after 5 cycles	[215]
Ag/AgCl/GO Ag/AgBr/GO	0.6 wt %	DP 71 % DP 85 %	No significant change in photocatalytic activity after 5 cycles	[216]
BiVO ₄ -G	No data	R_{H_2} 0.75 $\mu\text{mol h}^{-1}$	N.A.	[217]
TiO ₂ -G	wt % wt % 10 wt %	R_{H_2} 6.5 $\mu\text{mol h}^{-1}$ R_{H_2} 8.6 $\mu\text{mol h}^{-1}$ R_{H_2} 4.7 $\mu\text{mol h}^{-1}$	N.A.	[218]
InNbO ₄ -G	N.A.	Reaction rate 0.0346 min^{-1}	N.A.	[219]
MnFe ₂ O ₄ -GSC	100mg	DP 100% with H ₂ O ₂	99.97% efficiency after 5 cycles	[220]

Besides graphene-based composites of mono transition metal oxides, their bimetallic composites have also been extensively explored with the benefits of visible light driven photocatalysis. As the major portion of solar energy falls under visible light, it also improves the composite's efficiency [221]. Enhanced diffusion coefficient associated with graphene-based spinel oxides composite may prove beneficial for photocatalysis application [141,143]. Fu and Wang et al. reported visible light-driven MB degradation by ZnFe_2O_4 graphene composite [192]. Here, the magnetic property of ZnFe_2O_4 makes the composite magnetically discrete from the suspension system negating the requirement of additional magnetic components. Visible light irradiation of ZnFe_2O_4 graphene composite results in effective charge separation and generates strong oxidants via photoactive degradation of H_2O_2 with enhanced stability. Enhanced charge transfer of the composite is also demonstrated by a small radius of the semicircle in high frequency region of impedance plot compared to that of bare GO and ZnFe_2O_4 (Figure 8). Further, MnFe_2O_4 -graphene sand composite was used as photocatalyst against 100% MB degradation under sunlight irradiation [220]. The high performance resulted from simultaneous participation of Mn and Fe on the catalyst surface for the decomposing H_2O_2 and in the production of $\bullet\text{OH}$ favoring photogenerated carriers' separation in MnFe_2O_4 . Hydrothermal growth of graphene- BiWO_6 , reported by Gao et al. [222], shows enhanced photocatalytic degradation activity under RB's visible light. The interaction of graphene with BiWO_6 shifts the Fermi level and decrease the conduction band potential. Fu et al. reported the synergistic effect of CuFe_2O_4 nanoflakes and graphene sheets, resulting in superior photocatalytic performance. The possible mechanism of photocatalytic degradation takes place via the following steps:

Figure 8. (a) Uniform dispersion of ZnFe_2O_4 nanoparticles over graphene (b) Images of ZnFe_2O_4 graphene suspension with (1) and without (2) magnetic field, (c) EIS of (1) ZnFe_2O_4 graphene, (2) pure ZnFe_2O_4 and (3) GO and (d) stability test shown by photodegradation rate of MB using ZnFe_2O_4 -G for 10 cycles. Adapted with permission from [192]. Copyright 2011, American Chemical Society.

Here, the generated active species oxidize MB molecules which are adsorbed on CuFe_2O_4 graphene composite via π - π or electrostatic interaction. $\text{CuBi}_2\text{O}_4/\text{G}$ was also evaluated for their photocatalytic performance after their synthesis by solvothermal method [223]. They possess 95% and 85% degradation efficiency towards degradation of MB and MO compared to pristine CuBi_2O_4 . Visible light irradiation of CuBi_2O_4 result in the generation of electrons and holes on the surface followed by transference of photoexcited electrons to graphene sheets by percolation mechanism. Then, negatively charged graphene activates oxygen to form superoxide anion radicals and holes, which are adsorbed by water to produce hydroxyl radicals. Active species generated by graphene then oxidizes the dye molecule (adsorbed on the CuBi_2O_4 -graphene active sites) and hence, increases the photocatalytic degradation rate of dyes from industrial effluents. These new adsorbents ensure visible light-driven dye degradation with large adsorption capacity and electron/hole recombination lifetime.

4. Conclusions and Perspectives

Photocatalysis is an imperative route for greener decipher of energy and environmental issues of modern era. Catalytic efficiency of various photocatalysts has been altered by employing different techniques by the researchers. This review has given stress over different adsorbents based on transition metal oxides, bimetallic oxides and their carbon composites for photocatalysis. Different approaches regarding synthetic technique, heterostructure, etc. led to augmented adsorptivity, light absorption intensity, electron/hole pair lifetime with extended light adsorption range which may unlock various breaks for the next generation photocatalysts. These approaches have been proved good but no one proved a panacea. However, the mechanistic description is still lacking and vigilant designs of the functional materials are vital for rational progress. It is worthy to note that although great improvements have been accomplished by utilizing the “rising star: graphene” in photocatalysis, still there are some challenges for full exploitation of graphene-based composites.

In addition to the above tactics to enhance photocatalysis, the deficiency in analogous results among various studies of photocatalysis led to a great challenge, in spite of a large amount of literature. Recently, the progress has been made on the utilization of nanocarbons for existing photocatalyst which improves the photocatalytic activity in a broad spectrum. Further, the photocatalysts’ development and endorsement depend on the harmonic growth of academia and industrial revolution, particularly for the optimal testing condition and methods for dye degradation. The intensive efforts from systematic amalgamation of academicians research worldwide would bring revolt in developing potential photocatalysts for dye degradation.

Author Contributions: P.A. (Preety Ahuja) and S.K.U.; writing original draft preparation, S.K.U., R.K. and P.A. (Pankaj Attri); review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: Preety Ahuja acknowledges NPDF (project no. PDF/2015/000470) from the Department of Science and Technology, India; Pankaj Attri is thankful to JSPS-KAKENHI grant number 20K14454.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wang, Y.; Sun, X.; Xian, T.; Liu, G.; Yang, H. Photocatalytic degradation of simulated dye wastewater in different pH environments by using $\text{BaTiO}_3/\text{Bi}_2\text{WO}_6$ heterojunction photocatalysts. *Opt. Mat.* **2021**, *113*, 110853. [CrossRef]
2. Ning, L.; Xukai, L.; Mengting, H.; Xiaoguang, D.; Beibei, Y.; Guanyi, C.; Shaobin, W. Catalytic membrane-based oxidation-filtration systems for organic wastewater purification: A review. *J. Hazard. Mater.* **2021**, *414*, 125478.
3. Jaspal, D.; Malviya, A. Composites for wastewater purification: A review. *Chemosphere* **2020**, *246*, 125788. [CrossRef]
4. Chan, S.H.S.; Wu, T.Y.; Juan, J.C.; Teh, C.Y. Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye wastewater. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 1130–1158. [CrossRef]
5. Waters, B.D. The Regulator’s View. In *Colour in Dye House Effluent*; Cooper, P., Ed.; The Society of Dyers and Colourists: Bradford, UK, 1995; pp. 22–30.

6. Pereira, A.G.B.; Rodrigues, F.H.A.; Paulino, A.T.; Martins, A.F.; Fajardo, A.R. Recent advances on composite hydrogels designed for the remediation of dye-contaminated water and wastewater: A review. *J. Clean. Prod.* **2021**, *284*, 124703. [\[CrossRef\]](#)
7. Banat, I.M.; Nigam, P.; Singh, D.; Marchant, R. Microbial decolorization of textile-dye-containing effluents: A review. *Bioresour. Technol.* **1996**, *58*, 217–227. [\[CrossRef\]](#)
8. Schwarzenbach, R.P.; Escher, B.I.; Fenner, K.; Hofstetter, T.B.; Johnson, C.A.; Gunten, U.V.; Wehrli, B. The Challenge of Micropollutants in Aquatic Systems. *Science* **2006**, *313*, 1072–1077. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Daneshvar, N.; Ashassi-Sorkhabi, H.; Tizpar, A. Decolorization of orange II by electrocoagulation method. *Sep. Purif. Technol.* **2003**, *31*, 153–162. [\[CrossRef\]](#)
10. Donkadolula, N.Y.; Kola, A.K.; Naz, I.; Saroj, D. A review on advanced physico-chemical and biological textile dye wastewater treatment techniques. *Rev. Environ. Sci. BioTechnol.* **2020**, *19*, 543–560. [\[CrossRef\]](#)
11. Kishor, R.; Purchase, D.; Saratale, G.D.; Saratale, R.G.; Ferreira, L.F.R.; Bilal, M.; Chandra, R.; Bhargava, R.N. Ecotoxicological and health concerns of persistent colouring pollutants of textile industry wastewater and treatment approaches for environmental safety. *J. Environ. Chem. Eng.* **2021**, *9*, 105012. [\[CrossRef\]](#)
12. Kadirvelu, K.; Kavipriya, M.; Karthika, C.; Radhika, M.; Vennilamani, N.; Pattabhi, S. Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour. Technol.* **2003**, *87*, 129–132. [\[CrossRef\]](#)
13. Baruah, S.; Dutta, J. Nanotechnology applications in pollution sensing and degradation in agriculture: A review. *Environ. Chem. Lett.* **2009**, *7*, 191–204. [\[CrossRef\]](#)
14. Choy, K.K.H.; McKay, G.; Porter, J.F. Resources, Sorption of acid dyes from effluents using activated carbon. *Resour. Conserv. Recycl.* **1999**, *27*, 57–71. [\[CrossRef\]](#)
15. Crini, G. Non-conventional low-cost adsorbents for dye removal: A review. *Bioresour. Technol.* **2006**, *97*, 1061–1085. [\[CrossRef\]](#)
16. Gupta, V.K.; Suhas. Application of low-cost adsorbents for dye removal—A review. *J. Environ. Manag.* **2009**, *90*, 2313–2342. [\[CrossRef\]](#)
17. Carvalho, M.C.; Pereira, C.; Gonçalves, I.C.; Pinheiro, H.M.; Santos, A.R.; Lopes, A.; Ferra, M.I. Assessment of the biodegradability of a monosulfonated azo dye and aromatic amines. *Int. Biodeterior. Biodegrad.* **2008**, *62*, 96–103. [\[CrossRef\]](#)
18. Lin, J.; Zhang, X.; Li, Z.; Lei, L. Biodegradation of Reactive blue 13 in a two-stage anaerobic/aerobic fluidized beds system with a *Pseudomonas* sp. isolate. *Bioresour. Technol.* **2010**, *101*, 34–40. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Wafaa, M.A.E.-R.; Hassan, M.; Khalafallah, M. Microflora involved in textile dye waste removal. *J. Basic Microbiol.* **2003**, *43*, 167–174.
20. Ambrósio, S.T.; Campos-Takaki, G.M. Decolorization of reactive azo dyes by *Cunninghamella elegans* UCP 542 under co-metabolic conditions. *Bioresour. Technol.* **2004**, *91*, 69–75. [\[CrossRef\]](#)
21. Chander, M.; Arora, D.S. Evaluation of some white-rot fungi for their potential to decolourize industrial dyes. *Dyes Pigm.* **2007**, *72*, 192–198. [\[CrossRef\]](#)
22. Wesenberg, D.; Kyriakides, I.; Agathos, S.N. White-rot fungi and their enzymes for the treatment of industrial dye effluents. *Biotechnol. Adv.* **2003**, *22*, 161–187. [\[CrossRef\]](#)
23. Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* **2001**, *77*, 247–255. [\[CrossRef\]](#)
24. Lourenco, N.D.; Novais, J.M.; Pinheiro, H.M. Reactive textile dye colour removal in a sequencing batch reactor. *Water Sci. Technol.* **2000**, *42*, 321–328. [\[CrossRef\]](#)
25. Gürses, A.; Yalçın, M.; Dogar, C. Electrocoagulation of some reactive dyes: A statistical investigation of some electrochemical variables. *Waste Manag.* **2002**, *22*, 491–499. [\[CrossRef\]](#)
26. Hao, O.J.; Kim, H.; Chiang, P.C. Decolorization of Wastewater. *Crit. Rev. Environ. Sci. Technol.* **2000**, *30*, 449–505. [\[CrossRef\]](#)
27. Ullah, R.; Dutta, J. Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles. *J. Hazard. Mater.* **2008**, *156*, 194–200. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Danish, M.S.S.; Estrella, L.L.; Alemaida, I.M.A.; Lisin, A.; Moiseev, N.; Ahmadi, M.; Nazari, M.; Wali, M.; Zaheb, H.; Senjyu, T. Photocatalytic Applications of Metal Oxides for Sustainable Environmental Remediation. *Metals* **2021**, *11*, 80. [\[CrossRef\]](#)
29. Gautam, S.; Agrawal, H.; Thakur, M.; Akbari, A.; Sharda, H.; Kaur, R.; Amini, M. Metal oxides and metal organic frameworks for the photocatalytic degradation: A review. *J. Environ. Chem. Eng.* **2020**, *8*, 103726. [\[CrossRef\]](#)
30. Zhu, J.; Jiang, Z. Electrochemical Photocatalytic Degradation of Eriochrome Black T Dye Using Synthesized TiO₂@CNTs Nanofibers. *Int. J. Electrochem. Sci.* **2021**, *16*, 210318. [\[CrossRef\]](#)
31. Sukri, S.N.A.M.; Shameli, K.; Isa, E.D.M.; Ismail, N.A. Green Synthesis of Zinc Oxide-Based Nanomaterials for Photocatalytic Studies: A Mini Review. *IOP Conf. Ser. Mater. Sci. Eng.* **2021**, *1051*, 012083. [\[CrossRef\]](#)
32. Thiruvengatachari, R.; Vigneswaran, S.; Moon, I.S. A review on UV/TiO₂ photocatalytic oxidation process. *Korean J. Chem. Eng.* **2008**, *25*, 64–72. [\[CrossRef\]](#)
33. Ahmed, S.; Rasul, M.G.; Martens, W.N.; Brown, R.; Hashib, M.A. Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewater: A review. *Water Air Soil Pollut.* **2011**, *215*, 3–29. [\[CrossRef\]](#)
34. Malato, S.; Fernández-Ibáñez, P.; Maldonado, M.I.; Blanco, J.; Gernjak, W. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catal. Today* **2009**, *147*, 1–59. [\[CrossRef\]](#)
35. Woods-Robinson, R.; Han, Y.; Zhang, H.; Ablekim, T.; Khan, I.; Persson, K.A.; Zakutayev, A. Wide Band Gap Chalcogenide Semiconductors. *Chem. Rev.* **2020**, *120*, 4007–4055. [\[CrossRef\]](#) [\[PubMed\]](#)

36. Gupta, S.M.; Tripathi, M. A review of TiO₂ nanoparticles. *Chi. Sci. Bull.* **2011**, *56*, 1639–1657. [\[CrossRef\]](#)
37. Carp, O.; Huisman, C.L.; Reller, A. Photoinduced reactivity of titanium dioxide. *Prog. Solid State Chem.* **2004**, *32*, 33–177. [\[CrossRef\]](#)
38. Sun, H.; Liu, S.; Liu, S.; Wang, S. A comparative study of reduced graphene oxide modified TiO₂, ZnO and Ta₂O₅ in visible light photocatalytic/photochemical oxidation of methylene blue. *Appl. Catal. B* **2014**, *146*, 162–168. [\[CrossRef\]](#)
39. Haneda, D.L.H. Synthesis of nitrogen-containing ZnO powders by spray pyrolysis and their visible-light photocatalysis in gas-phase acetaldehyde decomposition. *J. Photochem. Photobiol. A* **2003**, *155*, 171–178.
40. Yang, G.C.C.; Chan, S.W. Photocatalytic reduction of chromium(VI) in aqueous solution using dye-sensitized nanoscale ZnO under visible light irradiation. *J. Nanopart. Res.* **2009**, *11*, 221–230. [\[CrossRef\]](#)
41. Huang, Y.; Wei, Y.; Wu, J.; Guo, C.; Wang, M.; Yin, S.; Sato, T. Low temperature synthesis and photocatalytic properties of highly oriented ZnO/TiO_{2-x}N_y coupled photocatalysts. *Appl. Catal. B* **2012**, *123–124*, 9–17. [\[CrossRef\]](#)
42. Maleh, H.K.; Kumar, B.G.; Rajendran, S.; Qin, J.; Vadivel, S.; Durgalakshmi, D.; Gracia, F.; Soto-Moscoso, M.; Orooji, Y.; Karimi, F. Tuning of metal oxides photocatalytic performance using Ag nanoparticles integration. *J. Mol. Liq.* **2020**, *314*, 113588. [\[CrossRef\]](#)
43. Karthikeyan, C.; Arunachalam, P.; Ramachandran, K.; Al-Mayouf, A.M.; Karupuchamy, S. Recent advances in semiconductor metal oxides with enhanced methods for solar photocatalytic applications. *J. Alloys Compd.* **2020**, *828*, 154281. [\[CrossRef\]](#)
44. Oyewo, O.A.; Elemike, E.E.; Onwudiwe, D.C.; Onyango, M.S. Metal oxide-cellulose nanocomposites for the removal of toxic metals and dyes from wastewater. *Int. J. Biol. Macromol.* **2020**, *164*, 2477–2496. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38. [\[CrossRef\]](#)
46. Li, C.; Yuan, J.; Han, B.; Shanguan, W. Synthesis and photochemical performance of morphology-controlled CdS photocatalysts for hydrogen evolution under visible light. *Int. J. Hydrogen Energy* **2011**, *36*, 4271–4279. [\[CrossRef\]](#)
47. Fujita, E.; Muckerman, J.T.; Domen, K. Editorial: A current perspective on photocatalysis. *ChemSuschem* **2011**, *4*, 155–157. [\[CrossRef\]](#)
48. Hermann, J.M. Fundamentals and misconceptions in photocatalysis. *J. Photochem. Photobiol. A* **2010**, *216*, 85–93. [\[CrossRef\]](#)
49. Fujishima, A.; Zhang, X. Titanium dioxide photocatalysis: Present situation and future approaches. *Comptes Rendus Chim.* **2006**, *9*, 750–760. [\[CrossRef\]](#)
50. Zhao, D.; Chen, C.; Wang, Y.; Ma, W.; Zhao, J.; Rajh, T.; Zang, L. Enhanced photocatalytic degradation of dye pollutants under visible irradiation on Al(III)-modified TiO₂: Structure, interaction, and interfacial electron transfer. *Environ. Sci. Technol.* **2008**, *42*, 308–314. [\[CrossRef\]](#)
51. Yu, J.; Xiong, J.; Cheng, B.; Liu, S. Fabrication and characterization of Ag–TiO₂ multiphase nanocomposite thin films with enhanced photocatalytic activity. *Appl. Catal. B* **2005**, *60*, 211–221. [\[CrossRef\]](#)
52. Sung-Suh, H.M.; Choi, J.R.; Hah, H.J.; Koo, S.M.; Bae, Y.C. Comparison of Ag deposition effects on the photocatalytic activity of nanoparticulate TiO₂ under visible and UV light irradiation. *J. Photochem. Photobiol. A* **2004**, *163*, 37–44. [\[CrossRef\]](#)
53. Wilke, K.; Breuer, H.D. The influence of transition metal doping on the physical and photocatalytic properties of titania. *J. Photochem. Photobiol. A* **1999**, *121*, 49–53. [\[CrossRef\]](#)
54. Martin, S.T.; Morrison, C.L.; Hoffmann, M.R. Photochemical Mechanism of Size-Quantized Vanadium-Doped TiO₂ Particles. *J. Phys. Chem.* **1994**, *98*, 13695–13704. [\[CrossRef\]](#)
55. Choi, W.; Termin, A.; Hoffmann, M.R. The Role of Metal Ion Dopants in Quantum-Sized TiO₂: Correlation between Photoreactivity and Charge Carrier Recombination Dynamics. *J. Phys. Chem.* **1994**, *98*, 13669–13679. [\[CrossRef\]](#)
56. Klosek, S.; Raftery, D. Visible Light Driven V-Doped TiO₂ Photocatalyst and Its Photooxidation of Ethanol. *J. Phys. Chem. B* **2001**, *105*, 2815–2819. [\[CrossRef\]](#)
57. Sun, M.; Lin, T.; Cheng, G.; Ye, F.; Yu, L. Hydrothermal Synthesis of Boron-Doped MnO₂ and Its Decolorization Performance. *J. Nanomater.* **2014**, *2014*, 175924. [\[CrossRef\]](#)
58. Ksibi, M.; Rossignol, S.; Tatibouët, J.-M.; Trapalis, C. Synthesis and solid characterization of nitrogen and sulfur-doped TiO₂ photocatalysts active under near visible light. *Mater. Lett.* **2008**, *62*, 4204–4206. [\[CrossRef\]](#)
59. Du, P.; Bueno-Lopez, A.; Verbaas, M.; Almeida, A.R.; Makkee, M.; Moulijn, J.A.; Mul, G. The effect of surface OH-population on the photocatalytic activity of rare earth-doped P25-TiO₂ in methylene blue degradation. *J. Catal.* **2008**, *260*, 75–80. [\[CrossRef\]](#)
60. Zhu, J.; Xie, J.; Chen, M.; Jiang, D.; Wu, D. Low temperature synthesis of anatase rare earth doped titania-silica photocatalyst and its photocatalytic activity under solar-light. *Colloids Surf. A Physicochem. Eng. Asp.* **2010**, *355*, 178–182. [\[CrossRef\]](#)
61. Liu, R.; Wang, P.; Wang, X.; Yu, H.; Yu, J. UV- and Visible-Light Photocatalytic Activity of Simultaneously Deposited and Doped Ag/Ag(I)-TiO₂ Photocatalyst. *J. Phys. Chem. C* **2012**, *116*, 17721–17728. [\[CrossRef\]](#)
62. Suda, Y.; Kawasaki, H.; Ueda, T.; Ohshima, T. Preparation of high quality nitrogen doped TiO₂ thin film as a photocatalyst using a pulsed laser deposition method. *Thin Solid Films* **2004**, *453–454*, 162–166. [\[CrossRef\]](#)
63. Gole, J.L.; Stout, J.D.; Burda, C.; Lou, Y.; Chen, X. Highly Efficient Formation of Visible Light Tunable TiO_{2-x}N_x Photocatalysts and Their Transformation at the Nanoscale. *J. Phys. Chem. B* **2004**, *108*, 1230–1240. [\[CrossRef\]](#)
64. Miyauchi, M.; Ikezawa, A.; Tobimatsu, H.; Irie, H.; Hashimoto, K. Zeta potential and photocatalytic activity of nitrogen doped TiO₂ thin films. *Phys. Chem. Chem. Phys.* **2004**, *6*, 865–870. [\[CrossRef\]](#)
65. Hiromasa, T.; Masahiro, M. N-doped TiO₂ Nanotube with Visible Light Activity. *Chem. Lett.* **2004**, *33*, 1108–1109.
66. Wang, J.; Tafen, D.N.; Lewis, J.P.; Hong, Z.; Manivannan, A.; Zhi, M.; Li, M.; Wu, N. Origin of Photocatalytic Activity of Nitrogen-Doped TiO₂ Nanobelts. *J. Am. Chem. Soc.* **2009**, *131*, 12290–12297. [\[CrossRef\]](#)

67. Emeline, A.V.; Kuznetsov, V.N.; Rubchuk, V.K.; Serpone, N. Visible-Light-Active Titania Photocatalysts: The Case of N-Doped TiO₂ S—Properties and Some Fundamental Issues. *Int. J. Photoenergy* **2008**, *2008*, 258394. [\[CrossRef\]](#)
68. Wu, Z.; Dong, F.; Liu, Y.; Wang, H. Enhancement of the visible light photocatalytic performance of C-doped TiO₂ by loading with V₂O₅. *Catal. Commun.* **2009**, *11*, 82–86. [\[CrossRef\]](#)
69. Daneshvar, N.; Salari, D.; Khataee, A.R. Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂. *J. Photochem. Photobiol. A* **2004**, *162*, 317–322. [\[CrossRef\]](#)
70. Moussavi, G.; Mahmoudi, M. Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles. *J. Hazard. Mater.* **2009**, *168*, 806–812. [\[CrossRef\]](#)
71. El-Hankari, S.; Aguilera-Sigalat, J.; Bradshaw, D. Surfactant-assisted ZnO processing as a versatile route to ZIF composites and hollow architectures with enhanced dye adsorption. *J. Mater. Chem. A* **2016**, *4*, 13509–13518. [\[CrossRef\]](#)
72. Kaliraj, L.; Ahn, J.C.; Rupa, E.J.; Abid, S.; Lu, J.; Yang, D.C. Synthesis of panos extract mediated ZnO nano-flowers as photocatalyst for industrial dye degradation by UV illumination. *J. Photochem. Photobiol. B* **2019**, *199*, 111588. [\[CrossRef\]](#)
73. Vinayagam, R.; Selvaraj, R.; Arivalagan, P.; Varadavenkatesan, T. Synthesis, characterization and photocatalytic dye degradation capability of Calliandra haematocephala-mediated zinc oxide nanoflowers. *J. Photochem. Photobiol. B* **2020**, *203*, 111760. [\[CrossRef\]](#)
74. Moghaddas, S.M.T.H.; Elahi, B.; Javanbakht, V. Biosynthesis of pure zinc oxide nanoparticles using Quince seed mucilage for photocatalytic dye degradation. *J. Alloys Compd.* **2020**, *821*, 153519. [\[CrossRef\]](#)
75. Kalpana, V.N.; Kataru, B.A.S.; Sravani, N.; Vigneshwari, T.; Panneerselvam, A.; Rajeswari, V.D. Biosynthesis of zinc oxide nanoparticles using culture filtrates of *Aspergillus niger*: Antimicrobial textiles and dye degradation studies. *Open Nano* **2018**, *3*, 48–55. [\[CrossRef\]](#)
76. Meng, A.; Xing, J.; Li, Z.; Li, Q. Cr-doped ZnO nanoparticles: Synthesis, characterization, adsorption property, and recyclability. *ACS Appl. Mater. Interfaces* **2015**, *7*, 27449–27457. [\[CrossRef\]](#) [\[PubMed\]](#)
77. Feng, W.; Nansheng, D.; Helin, H. Degradation mechanism of azo dye CI reactive red 2 by iron powder reduction and photooxidation in aqueous solutions. *Chemosphere* **2000**, *41*, 1233–1238. [\[CrossRef\]](#)
78. Khedr, M.H.; Abdel Halim, K.S.; Soliman, N.K. Synthesis and photocatalytic activity of nano-sized iron oxides. *Mater. Lett.* **2009**, *63*, 598–601. [\[CrossRef\]](#)
79. Kusior, A.; Michalec, K.; Jelen, P.; Radecka, M. Shaped Fe₂O₃ nanoparticles-Synthesis and enhanced photocatalytic degradation towards RhB. *Appl. Surf. Sci.* **2019**, *476*, 342–352. [\[CrossRef\]](#)
80. Shenoy, M.R.; Ayyasamy, S.; Reddy, M.V.V.; Kadarkarai, G.; Suryakanth, J.; Tamilarasan, S.; Thangavelu, S.; Jeyaramane, A.C. The effect of morphology-dependent surface charges of iron oxide on the visible light photocatalytic degradation of methylene blue dye. *J. Mater. Sci. Mater. Electron.* **2020**, *31*, 17703–17717. [\[CrossRef\]](#)
81. Kouhbanani, M.A.J.; Beheshtkhoo, N.; Taghizadeh, S.; Amani, A.M.; Alimardani, V. One-step green synthesis and characterization of iron oxide nanoparticles using aqueous leaf extract of *Teucrium polium* and their catalytic application in dye degradation. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2019**, *10*, 15007. [\[CrossRef\]](#)
82. Bishnoi, S.; Kumar, A.; Selvaraj, R. Facile synthesis of magnetic iron oxide nanoparticles using inedible *Cynometra ramiflora* fruit extract waste and their photocatalytic degradation of methylene blue dye. *Mater. Res. Bull.* **2018**, *97*, 121–127. [\[CrossRef\]](#)
83. Bibi, I.; Nazar, N.; Ata, S.; Sultan, M.; Ali, A.; Abbas, A.; Jilani, K.; Kamal, S.; Sarim, F.M.; Khan, M.I.; et al. Green synthesis of iron oxide nanoparticles using pomegranate seeds extract and photocatalytic activity evaluation for the degradation of textile dye. *J. Mater. Res. Technol.* **2019**, *8*, 6115–6124. [\[CrossRef\]](#)
84. Anchan, S.; Pai, S.; Sridevi, H.; Varadavenkatesan, T.; Vinayagam, R.; Selvaraj, R. Biogenic synthesis of ferric oxide nanoparticles using the leaf extract of *Peltophorum pterocarpum* and their catalytic dye degradation potential. *Biocatal. Agric. Biotechnol.* **2019**, *20*, 101251. [\[CrossRef\]](#)
85. Wang, C.-T. Photocatalytic activity of nanoparticle gold/iron oxide aerogels for azo dye degradation. *J. Non-Cryst. Solids* **2007**, *353*, 1126–1133. [\[CrossRef\]](#)
86. Mills, A.; Hunte, S.L. An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A Chem.* **1997**, *108*, 1–35. [\[CrossRef\]](#)
87. Guo, S.Y.; Han, S.; Chi, B.; Pu, J.; Li, J. A facile low-temperature approach to designing controlled amorphous-based titania composite photocatalysts with excellent noble-metal-free photocatalytic hydrogen production. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4743–4751. [\[CrossRef\]](#) [\[PubMed\]](#)
88. Zhang, Y.X.; Guo, X.L.; Huang, M.; Hao, X.D.; Yuan, Y.; Hua, C. Engineering birnessite-type MnO₂ nanosheets on fiberglass for pH-dependent degradation of methylene blue. *J. Phys. Chem. Solids* **2015**, *83*, 40–46. [\[CrossRef\]](#)
89. Pandit, A.A.; Pawar, R.A.; Shinde, D.R. Colloidal MnO₂ catalyzed degradation of two azo dyes methyl red and methyl orange from aqueous medium. *Int. J. Eng. Res.* **2013**, *4*, 1119–1122.
90. Liu, Y.; Chen, Z.; Shek, C.H.; Wu, C.M.L.; Lai, J.K.L. Hierarchical Mesoporous MnO₂ Superstructures Synthesized by Soft-Interface Method and Their Catalytic Performances. *ACS Appl. Mater. Interfaces* **2014**, *6*, 9776–9784. [\[CrossRef\]](#)
91. Ranjit, K.T.; Willner, I.; Bossmann, S.; Braun, A. Iron(III) Phthalocyanine-Modified Titanium Dioxide: A Novel Photocatalyst for the Enhanced Photodegradation of Organic Pollutants. *J. Phys. Chem. B* **1998**, *102*, 9397–9403. [\[CrossRef\]](#)
92. Iliev, V. Phthalocyanine-modified titania—Catalyst for photooxidation of phenols by irradiation with visible light. *J. Photochem. Photobiol. A: Chem.* **2002**, *151*, 195–199. [\[CrossRef\]](#)

93. Mele, G.; Sole, R.D.; Vasapollo, G.; García-López, E.; Palmisano, L.; Schiavello, M. Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO₂ impregnated with functionalized Cu(II)–porphyrin or Cu(II)–phthalocyanine. *J. Catal.* **2003**, *217*, 334–342. [\[CrossRef\]](#)
94. Yu, J.C.; Xie, Y.; Tang, H.Y.; Zhang, L.; Chan, H.C.; Zhao, J. Visible light-assisted bactericidal effect of metalphthalocyanine-sensitized titanium dioxide films. *J. Photochem. Photobiol. A Chem.* **2003**, *156*, 235–241. [\[CrossRef\]](#)
95. Kumar, S.G.; Devi, L.G. Review on Modified TiO₂ Photocatalysis under UV/Visible Light: Selected Results and Related Mechanisms on Interfacial Charge Carrier Transfer Dynamics. *J. Phys. Chem. A* **2011**, *115*, 13211–13241. [\[CrossRef\]](#) [\[PubMed\]](#)
96. Linsebigler, A.L.; Lu, G.; Yates, J.T., Jr. Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95*, 735–758. [\[CrossRef\]](#)
97. Shang, J.; Yao, W.; Zhu, Y.; Wu, N. Structure and photocatalytic performances of glass/SnO₂/TiO₂ interface composite film. *Appl. Catal. A Gen.* **2004**, *257*, 25–32. [\[CrossRef\]](#)
98. Shi, L.; Li, C.; Gu, H.; Fang, D. Morphology and properties of ultrafine SnO₂–TiO₂ coupled semiconductor particles. *Mater. Chem. Phys.* **2000**, *62*, 62–67. [\[CrossRef\]](#)
99. Omrani, N.; Nezamzadeh-Ejhieh, A. A comprehensive study on the enhanced photocatalytic activity of Cu₂O/BiVO₄/WO₃ nanoparticles. *J. Photochem. Photobiol. A* **2020**, *389*, 112223. [\[CrossRef\]](#)
100. Khalid, N.R.; Bilal, M.; Tahir, M.B.; Shakil, M.; Iqbal, T.; Rafique, M.; Yousaf, N.; Gillani, S.S.A. Interfacial coupling effect of Ag₂O nanorods over MoS₂ microflowers for improved photocatalytic activity. *Ceram. Int.* **2020**, *46*, 6856–6859. [\[CrossRef\]](#)
101. Irie, H.; Watanabe, Y.; Hashimoto, K. Nitrogen-Concentration Dependence on Photocatalytic Activity of TiO₂-xNx Powders. *J. Phys. Chem. B* **2003**, *107*, 5483–5486. [\[CrossRef\]](#)
102. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* **2001**, *293*, 269–271. [\[CrossRef\]](#)
103. Wu, T.; Liu, G.; Zhao, J.; Hidaka, H.; Serpone, N. Evidence for H₂O₂ Generation during the TiO₂-Assisted Photodegradation of Dyes in Aqueous Dispersions under Visible Light Illumination. *J. Phys. Chem. B* **1999**, *103*, 4862–4867. [\[CrossRef\]](#)
104. Belhekar, A.A.; Awate, S.V.; Anand, R. Photocatalytic activity of titania modified mesoporous silica for pollution control. *Catal. Commun.* **2002**, *3*, 453–458. [\[CrossRef\]](#)
105. Scaria, J.; Nidheesh, P.V.; Kumar, M.S. Synthesis and applications of various bimetallic nanomaterials in water and wastewater treatment. *J. Environ. Manag.* **2020**, *259*, 110011. [\[CrossRef\]](#)
106. Mahmood, M.A.; Baruah, S.; Dutta, J. Enhanced visible light photocatalysis by manganese doping or rapid crystallization with ZnO nanoparticles. *Mater. Chem. Phys.* **2011**, *130*, 531–535. [\[CrossRef\]](#)
107. Deka, S.; Joy, P.A. Synthesis and magnetic properties of Mn doped ZnO nanowires. *Solid State Commun.* **2007**, *142*, 190–194. [\[CrossRef\]](#)
108. Bhati, I.; Sharma, J.; Ameta, A.; Ameta, S.C. Synthesis and characterization of nanosized CeCr₂O₅ and its use as a photocatalyst. *Int. J. Chem. Sci.* **2011**, *9*, 1787–1796.
109. Liu, Y.; Sun, D. Effect of CeO₂ doping on catalytic activity of Fe₂O₃/γ-Al₂O₃ catalyst for catalytic wet peroxide oxidation of azo dyes. *J. Hazard. Mater.* **2007**, *143*, 448–454. [\[CrossRef\]](#)
110. Saravanan, R.; Karthikeyan, N.; Govindan, S.; Narayanan, V.; Stephen, A. Photocatalytic degradation of organic dyes using ZnO/CeO₂ nanocomposite material under visible light. *Adv. Mat. Res.* **2012**, *584*, 381–385.
111. Yang, X.; Wang, Y.; Xu, L.; Yu, X.; Guo, Y. Silver and Indium Oxide Codoped TiO₂ Nanocomposites with Enhanced Photocatalytic Activity. *J. Phys. Chem. C* **2008**, *112*, 11481–11489. [\[CrossRef\]](#)
112. Georgekutty, R.; Seery, M.K.; Pillai, S.C. A Highly Efficient Ag-ZnO Photocatalyst: Synthesis, Properties, and Mechanism. *J. Phys. Chem. C* **2008**, *112*, 13563–13570. [\[CrossRef\]](#)
113. Ganesan, M.; Viswanathan, B.; Viswanath, R.P.; Varadarajan, T.K. Photocatalytic behavior of CeO₂-TiO₂ system for the degradation of methylene blue. *Indian J. Chem.* **2009**, *48*, 480–488.
114. Xu, D.; Cheng, F.; Lu, Q.; Dai, P. Microwave Enhanced Catalytic Degradation of Methyl Orange in Aqueous Solution over CuO/CeO₂ Catalyst in the Absence and Presence of H₂O₂. *Ind. Eng. Chem. Res.* **2014**, *53*, 2625–2632. [\[CrossRef\]](#)
115. Tung, W.S.; Daoud, W.A. New approach toward nanosized ferrous ferric oxide and Fe₃O₄-doped titanium dioxide photocatalysts. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2453–2461. [\[CrossRef\]](#) [\[PubMed\]](#)
116. Zhu, J.; Zheng, W.; Hea, B.; Jhang, J.; Anpo, M. Characterization of Fe–TiO₂ photocatalysts synthesized by hydrothermal method and their photocatalytic reactivity for photodegradation of XRG dye diluted in water. *J. Mol. Catal. A Chem.* **2004**, *216*, 35–43. [\[CrossRef\]](#)
117. Zhang, L.; Lian, J.; Wu, L.; Duan, Z.; Jiang, J.; Zhao, L. Synthesis of a Thin-Layer MnO₂ Nanosheet-Coated Fe₃O₄ Nanocomposite as a Magnetically Separable Photocatalyst. *Langmuir* **2014**, *30*, 7006–7013. [\[CrossRef\]](#) [\[PubMed\]](#)
118. Sreethawong, T.; Ngamsinlapasathian, S.; Yoshikawa, S. Surfactant-aided sol–gel synthesis of mesoporous-assembled TiO₂–NiO mixed oxide nanocrystals and their photocatalytic azo dye degradation activity. *Chem. Eng. J.* **2012**, *192*, 292–300. [\[CrossRef\]](#)
119. Sreethawong, T.; Yoshikawa, S. Impact of photochemically deposited monometallic Pt and bimetallic Pt–Au nanoparticles on photocatalytic dye-sensitized H₂ production activity of mesoporous-assembled TiO₂–SiO₂ mixed oxide nanocrystal. *Chem. Eng. J.* **2012**, *197*, 272–282. [\[CrossRef\]](#)
120. Mohamed, R.M.; Mkhali, I.A.; Baeissa, E.S.; Al-Rayyani, M.A. Photocatalytic Degradation of Methylene Blue by Fe/ZnO/SiO₂ Nanoparticles under Visible light. *J. Nanotechnol.* **2012**, *2012*, 329082.

121. Xue, M.; Huang, L.; Wang, J.Q.; Wang, Y.; Gao, L.; Zhu, J.H.; Zhou, Z.G. The direct synthesis of mesoporous structured $\text{MnO}_2/\text{TiO}_2$ nanocomposite: A novel visible-light active photocatalyst with large pore size. *Nanotechnology* **2008**, *19*, 185604. [\[CrossRef\]](#)
122. Wang, C.; Shao, C.; Zhang, X.; Liu, Y. SnO_2 Nanostructures- TiO_2 Nanofibers Heterostructures: Controlled Fabrication and High Photocatalytic Properties. *Inorg. Chem.* **2009**, *48*, 7261–7268. [\[CrossRef\]](#) [\[PubMed\]](#)
123. Li, H.B.; Song, Y.D.; Chen, S.G. Preparation and Characterization of MnO_2 Loaded CuO Nanosheets. *Adv. Mat. Res.* **2013**, *652–654*, 241–244.
124. Qian, K.; Qian, Z.X.; Hua, Q.; Jiang, Z.Q.; Huang, W.X. Structure–activity relationship of CuO/MnO_2 catalysts in CO oxidation. *Appl. Surf. Sci.* **2013**, *273*, 357–363. [\[CrossRef\]](#)
125. Yang, Z.; Yang, Y.; Zhu, X.; Chen, G.; Zhang, W. An Outward Coating Route to CuO/MnO_2 Nanorod Array Films and Their Efficient Catalytic Oxidation of Acid Fuchsin Dye. *Ind. Eng. Chem. Res.* **2014**, *53*, 9608–9615. [\[CrossRef\]](#)
126. Guo, Y.; Yang, X.; Ma, F.; Li, K.; Xu, L.; Yuan, X.; Guo, Y. Additive-free controllable fabrication of bismuth vanadates and their photocatalytic activity toward dye degradation. *Appl. Surf. Sci.* **2010**, *256*, 2215–2222. [\[CrossRef\]](#)
127. Shang, M.; Wang, W.; Zhou, L.; Sun, S.; Yin, W. Nanosized BiVO_4 with high visible-light-induced photocatalytic activity: Ultrasonic-assisted synthesis and protective effect of surfactant. *J. Hazard. Mater.* **2009**, *172*, 338–344. [\[CrossRef\]](#)
128. Yin, W.; Wang, W.; Zhou, L.; Sun, S.; Zhang, L. CTAB-assisted synthesis of monoclinic BiVO_4 photocatalyst and its highly efficient degradation of organic dye under visible-light irradiation. *J. Hazard. Mater.* **2009**, *173*, 194–199. [\[CrossRef\]](#)
129. Ghorai, T.K.; Dhak, D.; Dalai, S.; Pramanik, P. Preparation and photocatalytic activity of nano-sized nickel molybdate (NiMoO_4) doped bismuth titanate ($\text{Bi}_2\text{Ti}_4\text{O}_{11}$) (NMBT) composite. *J. Alloys Compd.* **2008**, *463*, 390–397. [\[CrossRef\]](#)
130. Cruz, A.M.L.; Alfaro, S.O. Synthesis and characterization of $\gamma\text{-Bi}_2\text{MoO}_6$ prepared by co-precipitation: Photoassisted degradation of organic dyes under vis-irradiation. *J. Mol. Catal. A Chem.* **2010**, *320*, 85–91. [\[CrossRef\]](#)
131. Xu, X.; Ni, Q. Synthesis and characterization of novel $\text{Bi}_2\text{MoO}_6/\text{NaY}$ materials and photocatalytic activities under visible light irradiation. *Catal. Commun.* **2010**, *11*, 359–363. [\[CrossRef\]](#)
132. Sahoo, P.P.; Sumithra, S.; Madras, G.; Row, T.N.G. Synthesis, structure and photocatalytic properties of $\beta\text{-ZrMo}_2\text{O}_8$. *Bull. Mater. Sci.* **2009**, *32*, 337–342. [\[CrossRef\]](#)
133. Mulla, I.S.; Natarajan, N.; Gaikwad, A.B.; Samuel, V.; Guptha, U.N.; Ravi, V. A coprecipitation technique to prepare CoTa_2O_6 and CoNb_2O_6 . *Mater. Lett.* **2007**, *61*, 2127–2129. [\[CrossRef\]](#)
134. Machida, M.; Yabunaka, J.; Kijima, T. Synthesis and Photocatalytic Property of Layered Perovskite Tantalates, $\text{RbLnTa}_2\text{O}_7$ ($\text{Ln} = \text{La, Pr, Nd, and Sm}$). *Chem. Mater.* **2000**, *12*, 812–817. [\[CrossRef\]](#)
135. Eng, H.W.; Barnes, P.W.; Auer, B.M.; Woodward, P.M. Investigations of the electronic structure of d^0 transition metal oxides belonging to the perovskite family. *J. Solid State Chem.* **2003**, *175*, 94–109. [\[CrossRef\]](#)
136. Ullah, R.; Sun, H.; Ang, H.M.; Tadé, M.O.; Wang, S. Visible light photocatalytic degradation of organics on nanoparticles of bi-metallic oxides. *Sep. Purify. Technol.* **2012**, *89*, 98–106. [\[CrossRef\]](#)
137. Su, S.; Guo, W.; Leng, Y.; Yi, C.; Ma, Z. Heterogeneous activation of Oxone by $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanocatalysts for degradation of rhodamine B. *J. Hazard. Mater.* **2013**, *244–245*, 736–742. [\[CrossRef\]](#) [\[PubMed\]](#)
138. Yu, K.; Yang, S.; He, H.; Sun, C.; Gu, C.; Ju, Y. Visible light-driven photocatalytic degradation of rhodamine B over NaBiO_3 : Pathways and mechanism. *J. Phys. Chem. A* **2009**, *113*, 10024–10032. [\[CrossRef\]](#)
139. Li, S.J.; Ma, Z.; Wang, L.; Liu, J. Influence of MnO_2 on the photocatalytic activity of P-25 TiO_2 in the degradation of methyl orange. *Sci. China Ser. B Chem.* **2008**, *51*, 179–185. [\[CrossRef\]](#)
140. Ahuja, P.; Ujjain, S.K.; Sharma, R.K.; Singh, G. Enhanced supercapacitor performance by incorporating nickel in manganese oxide. *RSC Adv.* **2014**, *4*, 57192–57199. [\[CrossRef\]](#)
141. Ahuja, P.; Sharma, R.K.; Singh, G. Solid-state, high-performance supercapacitor using graphene nanoribbons embedded with zinc manganite. *J. Mater. Chem. A* **2015**, *3*, 4931–4937. [\[CrossRef\]](#)
142. Ujjain, S.K.; Ahuja, P.; Sharma, R.K. Graphene nanoribbon wrapped cobalt manganite nanocubes for high performance all-solid-state flexible supercapacitors. *J. Mater. Chem. A* **2015**, *3*, 9925–9931. [\[CrossRef\]](#)
143. Ahuja, P.; Sahu, V.; Ujjain, S.K.; Sharma, R.K.; Singh, G. Performance evaluation of Asymmetric Supercapacitor based on Cobalt manganite modified graphene nanoribbons. *Electrochim. Acta* **2014**, *146*, 429–436. [\[CrossRef\]](#)
144. Ahuja, P.; Ujjain, S.K.; Kanojia, R. Electrochemical behaviour of manganese & ruthenium mixed oxide@ reduced graphene oxide nanoribbon composite in symmetric and asymmetric supercapacitor. *Appl. Surf. Sci.* **2018**, *427*, 102–111.
145. Deori, K.; Ujjain, S.K.; Sharma, R.K.; Deka, S. Morphology Controlled Synthesis of Nanoporous Co_3O_4 Nanostructures and Their Charge Storage Characteristics in Supercapacitors. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10665–10672. [\[CrossRef\]](#)
146. Stoyanova, M.; Slavova, I.; Christoskova, S.; Ivanova, V. Catalytic performance of supported nanosized cobalt and iron–cobalt mixed oxides on MgO in oxidative degradation of Acid Orange 7 azo dye with peroxy monosulfate. *Appl. Catal. A Gen.* **2014**, *476*, 121–132. [\[CrossRef\]](#)
147. Wang, Y.; Sun, H.; Ang, H.M.; Tadé, M.O.; Wang, S. Facile Synthesis of Hierarchically Structured Magnetic $\text{MnO}_2/\text{ZnFe}_2\text{O}_4$ Hybrid Materials and Their Performance in Heterogeneous Activation of Peroxy monosulfate. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19914–19923. [\[CrossRef\]](#)
148. Sathishkumar, P.; Mangalaraja, R.V.; Anandan, S.; Ashokkumar, M. $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ nanocatalysts for the photocatalytic degradation of Reactive Red 120 in aqueous solutions in the presence and absence of electron acceptors. *Chem. Eng. J.* **2013**, *220*, 302–310. [\[CrossRef\]](#)

149. Cui, B.; Lin, H.; Liu, Y.; Li, J.; Sun, P.; Zhao, X.; Liu, C. Photophysical and Photocatalytic Properties of Core-Ring Structured NiCo_2O_4 Nanoplatelets. *J. Phys. Chem. C* **2009**, *113*, 14083–14087. [\[CrossRef\]](#)
150. Singh, M.K.; Patra, A. Highly efficient and Reusable ZnO microflower photocatalyst on stainless steel mesh under UV-Vis and natural sunlight. *Opt. Mater.* **2020**, *107*, 110000. [\[CrossRef\]](#)
151. Basnet, P.; Samanta, D.; Chenu, T.I.; Chatterjee, S. Visible light facilitated degradation of alternate dye solutions by highly reusable Mn-ZnO nano-photocatalyst. *J. Alloys Compd.* **2021**, *867*, 158870. [\[CrossRef\]](#)
152. Sharma, S.; Basu, S. Highly reusable visible light active hierarchical porous WO_3/SiO_2 monolith in centimeter length scale for enhanced photocatalytic degradation of toxic pollutants. *Sep. Purif. Technol.* **2020**, *231*, 115916. [\[CrossRef\]](#)
153. Janitabar-Darzi, S.; Mahjoub, A.R. Investigation of phase transformations and photocatalytic properties of sol-gel prepared nanostructured ZnO/TiO_2 composites. *J. Alloys Compd.* **2009**, *486*, 805–808. [\[CrossRef\]](#)
154. Sajjad, A.K.L.; Shamailla, S.; Tian, B.; Chen, F.; Zhang, J. Comparative studies of operational parameters of degradation of azo dyes in visible light by highly efficient WO_x/TiO_2 photocatalyst. *J. Hazard. Mater.* **2010**, *177*, 781–791. [\[CrossRef\]](#)
155. Ghasemi, S.; Rahimnejad, S.; Setayesh, S.R.; Rohani, S.; Golami, M.R. Transition metal ions effect on the properties and photocatalytic activity of nanocrystalline TiO_2 prepared in an ionic liquid. *J. Hazard. Mater.* **2009**, *172*, 1573–1578. [\[CrossRef\]](#)
156. Shen, W.; Li, Z.; Wang, H.; Liu, Y.; Guo, Q.; Zhang, Y. Photocatalytic degradation for methylene blue using zinc oxide prepared by codeposition and sol-gel methods. *J. Hazard. Mater.* **2008**, *152*, 172–175. [\[CrossRef\]](#)
157. Singh, J.; Rath, A.; Rawat, M.; Kumar, V.; Kim, K.-H. The effect of manganese doping on structural, optical, and photocatalytic activity of zinc oxide nanoparticles. *Compos. B. Eng.* **2019**, *166*, 361–370. [\[CrossRef\]](#)
158. Xu, C.; Wei, X.; Guo, Y.; Wu, H.; Ren, Z.; Xu, G.; Shen, G.; Han, G. Surfactant-free synthesis of Bi_2WO_6 multilayered disks with visible-light-induced photocatalytic activity. *Mater. Res. Bull.* **2009**, *44*, 1635–1641. [\[CrossRef\]](#)
159. Lin, S.; Chen, J.; Weng, X.; Yang, L.; Chen, X. Fabrication and photocatalysis of mesoporous ZnWO_4 with PAMAM as a template. *Mater. Res. Bull.* **2009**, *44*, 1102–1105. [\[CrossRef\]](#)
160. Seddigi, Z.S. Removal of Alizarin Yellow Dye from Water Using Zinc Doped WO_3 Catalyst. *Bull. Environ. Contam. Toxicol.* **2010**, *84*, 564–567. [\[CrossRef\]](#) [\[PubMed\]](#)
161. Cho, I.; Kwak, C.H.; Kim, D.W.; Lee, S.; Hong, K.S. Photophysical, Photoelectrochemical, and Photocatalytic Properties of Novel SnWO_4 Oxide Semiconductors with Narrow Band Gaps. *J. Phys. Chem. C* **2009**, *113*, 10647–10653. [\[CrossRef\]](#)
162. Ahmad, M.; Ahmed, E.; Ahmed, W.; Elhissi, A.; Hong, Z.L.; Khalid, N.R. Enhancing visible light responsive photocatalytic activity by decorating Mn-doped ZnO nanoparticles on graphene. *Ceram. Int.* **2014**, *40*, 10085–10097. [\[CrossRef\]](#)
163. Ahuja, P.; Ujjain, S.K.; Kanojia, R. MnOx/C nanocomposite: An insight on high-performance supercapacitor and non-enzymatic hydrogen peroxide detection. *Appl. Surf. Sci.* **2017**, *404*, 197–205. [\[CrossRef\]](#)
164. Ujjain, S.K.; Sahu, V.; Sharma, R.K.; Singh, G. High performance, all solid state, flexible supercapacitor based on ionic liquid functionalized graphene. *Electrochim. Acta* **2015**, *157*, 245–251. [\[CrossRef\]](#)
165. Ujjain, S.K.; Ahuja, P.; Sharma, R.K. Facile preparation of graphene nanoribbon/cobalt coordination polymer nanohybrid for non-enzymatic H_2O_2 sensing by dual transduction: Electrochemical and fluorescence. *J. Mater. Chem. B* **2015**, *3*, 7614–7622. [\[CrossRef\]](#)
166. Putri, A.D.; Chotimah, N.; Ujjain, S.K.; Wang, S.; Futamura, R.; Vallejos-Burgos, F.; Khoerunnisa, F.; Morimoto, M.; Wang, Z.; Hattori, Y.; et al. Charge-transfer mediated nanopore-controlled pyrene derivatives/graphene colloids. *Carbon* **2018**, *139*, 512–521. [\[CrossRef\]](#)
167. Ujjain, S.K.; Sharma, R.K.; Singh, G. Co_3O_4 @reduced graphene oxide nanoribbon for high performance asymmetric supercapacitor. *Electrochim. Acta* **2015**, *169*, 276–282. [\[CrossRef\]](#)
168. Ujjain, S.K.; Bagusetty, A.; Matsuda, Y.; Tanaka, H.; Ahuja, P.; De Tomas, C.; Sakai, M.; Vallejos-Burgos, F.; Futamura, R.; Suarez-Martinez, I.; et al. Adsorption separation of heavier isotope gases in subnanometer carbon pores. *Nat. Commun.* **2021**, *12*, 546. [\[CrossRef\]](#) [\[PubMed\]](#)
169. Li, Y.; Zhang, S.; Yu, Q.; Yin, W. The effects of activated carbon support on the structure and properties of TiO_2 nanoparticles prepared by a sol-gel method. *Appl. Surf. Sci.* **2007**, *253*, 9254–9258. [\[CrossRef\]](#)
170. Wang, X.; Hu, Z.; Chen, Y.; Zhao, G.; Liu, Y.; Wen, Z. A novel approach towards high-performance composite photocatalyst of TiO_2 deposited on activated carbon. *Appl. Surf. Sci.* **2009**, *255*, 3953–3958. [\[CrossRef\]](#)
171. Zhang, X.; Zhou, M.; Lei, L. Preparation of photocatalytic TiO_2 coatings of nanosized particles on activated carbon by AP-MOCVD. *Carbon* **2005**, *43*, 1700–1708. [\[CrossRef\]](#)
172. Zhang, X.; Zhou, M.; Lei, L. TiO_2 photocatalyst deposition by MOCVD on activated carbon. *Carbon* **2006**, *44*, 325–333. [\[CrossRef\]](#)
173. Ao, Y.; Xu, J.; Fu, D.; Yuan, C. A simple route for the preparation of anatase titania-coated magnetic porous carbons with enhanced photocatalytic activity. *Carbon* **2008**, *46*, 596–603. [\[CrossRef\]](#)
174. Velasco, L.F.; Ania, C.O. Role of activated carbon features on the photocatalytic degradation of phenol. *Appl. Surf. Sci.* **2010**, *256*, 5254–5258. [\[CrossRef\]](#)
175. Lee, D.K.; Kim, S.C.; Kim, S.J.; Chung, I.S.; Kim, S.W. Photocatalytic oxidation of microcystin-LR with TiO_2 -coated activated carbon. *Chem. Eng. J.* **2004**, *102*, 93–98. [\[CrossRef\]](#)
176. Yao, Y.; Li, G.; Ciston, S.; Lueptow, R.M.; Gray, K.A. Photoreactive TiO_2 /carbon nanotube composites: Synthesis and reactivity. *Environ. Sci. Technol.* **2008**, *42*, 4952–4957. [\[CrossRef\]](#)

177. Ahmmad, B.; Kusumoto, Y.; Somekawa, S.; Ikeda, M. Carbon nanotubes synergistically enhance photocatalytic activity of TiO₂. *Catal. Commun.* **2008**, *9*, 1410–1413. [\[CrossRef\]](#)
178. Xia, X.H.; Jia, Z.J.; Yu, Y.; Liang, Y.; Wang, Z.; Ma, L.L. Preparation of multi-walled carbon nanotube supported TiO₂ and its photocatalytic activity in the reduction of CO₂ with H₂O. *Carbon* **2007**, *45*, 717–721. [\[CrossRef\]](#)
179. Hoffmann, M.R.; Martin, S.T.; Choi, W.; Bahnemann, D.W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96. [\[CrossRef\]](#)
180. Liu, B.; Zeng, H.C. Carbon Nanotubes Supported Mesoporous Mesocrystals of Anatase TiO₂. *Chem. Mater.* **2008**, *20*, 2711–2718. [\[CrossRef\]](#)
181. Woan, K.; Pyrgiotakis, G.; Sigmund, W. Photocatalytic Carbon-Nanotube-TiO₂ Composites. *Adv. Mater.* **2009**, *21*, 2233–2239. [\[CrossRef\]](#)
182. Xiong, P.; Fu, Y.; Wang, L.; Wang, X. Multi-walled carbon nanotubes supported nickel ferrite: A magnetically recyclable photocatalyst with high photocatalytic activity on degradation of phenols. *Chem. Eng. J.* **2012**, *195–196*, 149–157. [\[CrossRef\]](#)
183. Fan, W.; Lai, Q.; Zhang, Q.; Wang, Y. Nanocomposites of TiO₂ and Reduced Graphene Oxide as Efficient Photocatalysts for Hydrogen Evolution. *J. Phys. Chem. C* **2011**, *115*, 10694–10701. [\[CrossRef\]](#)
184. Li, N.; Liu, C.; Zhen, C.; Li, F.; Zhang, L.; Cheng, H.M. Battery Performance and Photocatalytic Activity of Mesoporous Anatase TiO₂ Nanospheres/Graphene Composites by Template-Free Self-Assembly. *Adv. Funct. Mater.* **2011**, *21*, 1717–1722. [\[CrossRef\]](#)
185. Xiang, Q.; Yu, J.; Jaroniec, M. Graphene-based semiconductor photocatalysts. *Chem. Soc. Rev.* **2012**, *41*, 782–796. [\[CrossRef\]](#) [\[PubMed\]](#)
186. Li, B.; Cao, H. ZnO@graphene composite with enhanced performance for the removal of dye from water. *J. Mater. Chem.* **2011**, *21*, 3346–3349. [\[CrossRef\]](#)
187. Zhang, J.; Xiong, Z.; Zhao, X.S. Graphene–metal–oxide composites for the degradation of dyes under visible light irradiation. *J. Mater. Chem.* **2011**, *21*, 3634–3640. [\[CrossRef\]](#)
188. Du, J.; Lai, X.; Yang, N.; Zhai, J.; Kisailus, D.; Su, F.; Wang, D.; Jiang, L. Hierarchically ordered macro-mesoporous TiO₂-graphene composite films: Improved mass transfer, reduced charge recombination, and their enhanced photocatalytic activities. *ACS Nano* **2011**, *5*, 590–596. [\[CrossRef\]](#)
189. Chen, J.S.; Wang, Z.; Dong, X.C.; Chena, P.; Lou, X.W.D. Graphene-wrapped TiO₂ hollow structures with enhanced lithium storage capabilities. *Nanoscale* **2011**, *3*, 2158–2161. [\[CrossRef\]](#) [\[PubMed\]](#)
190. Wang, D.; Hoi, D.; Li, J.; Yang, Z.; Nie, Z.; Kou, R.; Hu, D.; Wang, C.; Saraf, L.V.; Zhang, J.; et al. Self-Assembled TiO₂–Graphene Hybrid Nanostructures for Enhanced Li-Ion Insertion. *ACS Nano* **2009**, *3*, 907–914. [\[CrossRef\]](#)
191. Park, Y.; Kang, S.; Choi, W. Exfoliated and reorganized graphite oxide on titania nanoparticles as an auxiliary co-catalyst for photocatalytic solar conversion. *Phys. Chem. Chem. Phys.* **2011**, *13*, 9425–9431. [\[CrossRef\]](#)
192. Fu, Y.; Wang, X. Magnetically Separable ZnFe₂O₄–Graphene Catalyst and its High Photocatalytic Performance under Visible Light Irradiation. *Ind. Eng. Chem. Res.* **2011**, *50*, 7210–7218. [\[CrossRef\]](#)
193. Mukherji, A.; Seger, B.; Lu, G.Q.M.; Wang, L. Nitrogen Doped Sr₂Ta₂O₇ Coupled with Graphene Sheets as Photocatalysts for Increased Photocatalytic Hydrogen Production. *ACS Nano* **2011**, *5*, 3483–3492. [\[CrossRef\]](#)
194. Shen, J.; Yan, B.; Shi, M.; Ma, H.; Lia, N.; Ye, M. One step hydrothermal synthesis of TiO₂-reduced graphene oxide sheets. *J. Mater. Chem.* **2011**, *21*, 3415–3421. [\[CrossRef\]](#)
195. Williams, G.; Seger, B.; Kamat, P.V. TiO₂–Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano* **2008**, *2*, 1487–1491. [\[CrossRef\]](#)
196. Williams, G.; Kamat, P.V. Graphene-semiconductor nanocomposites: Excited-state interactions between ZnO nanoparticles and graphene oxide. *Langmuir* **2009**, *25*, 13869–13873. [\[CrossRef\]](#) [\[PubMed\]](#)
197. Kamat, P.V. Graphene-Based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Carbon Support. *J. Phys. Chem. Lett.* **2010**, *1*, 520–527. [\[CrossRef\]](#)
198. Lightcap, I.V.; Kosel, T.H.; Kamat, P.V. Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide. *Nano Lett.* **2010**, *10*, 577–583. [\[CrossRef\]](#)
199. Liu, J.; Bai, H.; Wang, Y.; Liu, Z.; Zhang, X.; Sun, D.D. Self-Assembling TiO₂ Nanorods on Large Graphene Oxide Sheets at a Two-Phase Interface and Their Anti-Recombination in Photocatalytic Applications. *Adv. Funct. Mater.* **2010**, *23*, 4175–4181. [\[CrossRef\]](#)
200. Zhou, K.; Zhu, Y.; Yang, X.; Jianga, X.; Lia, C. Preparation of graphene–TiO₂ composites with enhanced photocatalytic activity. *New J. Chem.* **2011**, *35*, 353–359. [\[CrossRef\]](#)
201. Yao, Y.; Yang, Z.; Sun, H.; Wang, S. Hydrothermal Synthesis of Co₃O₄–Graphene for Heterogeneous Activation of Peroxymonosulfate for Decomposition of Phenol. *Ind. Eng. Chem. Res.* **2012**, *51*, 14958–14965. [\[CrossRef\]](#)
202. Yao, Y.; Xu, C.; Yu, S.; Zhang, D.; Wang, S. Facile Synthesis of Mn₃O₄–Reduced Graphene Oxide Hybrids for Catalytic Decomposition of Aqueous Organics. *Ind. Eng. Chem. Res.* **2013**, *52*, 3637–3645. [\[CrossRef\]](#)
203. Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J. P25-Graphene Composite as a High Performance Photocatalyst. *ACS Nano* **2010**, *4*, 380–386. [\[CrossRef\]](#) [\[PubMed\]](#)
204. Fatima, R.; Warsi, M.F.; Zulfiqar, S.; Ragab, S.A.; Shakir, I.; Sarwar, M.I. Nanocrystalline transition metal oxides and their composites with reduced graphene oxide and carbon nanotubes for photocatalytic applications. *Ceram. Int.* **2020**, *46*, 16480–16492. [\[CrossRef\]](#)

205. Zhang, Y.; Tang, Z.; Fu, X.; Xu, Y. TiO₂–Graphene Nanocomposites for Gas-Phase Photocatalytic Degradation of Volatile Aromatic Pollutant: Is TiO₂–Graphene Truly Different from Other TiO₂–Carbon Composite Materials. *ACS Nano* **2010**, *4*, 7303–7314. [[CrossRef](#)] [[PubMed](#)]
206. Bai, X.; Wang, L.; Zong, R.; Lv, Y.; Sun, Y.; Zhu, Y. Performance Enhancement of ZnO Photocatalyst via Synergic Effect of Surface Oxygen Defect and Graphene Hybridization. *Langmuir* **2013**, *29*, 3097–3105. [[CrossRef](#)]
207. Li, X.; Yang, S.; Sun, J.; He, P.; Xu, X.; Ding, G. Tungsten oxide nanowire-reduced graphene oxide aerogel for high-efficiency visible light photocatalysis. *Carbon* **2014**, *78*, 38–48. [[CrossRef](#)]
208. Qu, J.; Shi, L.; He, C.; Gao, F.; Li, B.; Zhou, Q.; Hu, H.; Shao, G.; Wang, X.; Qiu, J. Highly efficient synthesis of graphene/MnO₂ hybrids and their application for ultrafast oxidative decomposition of methylene blue. *Carbon* **2014**, *66*, 485–492. [[CrossRef](#)]
209. Rani, S.; Kumar, M.; Sharma, S.; Kumar, D.; Tyagi, S. Effect of Graphene in Enhancing the Photo Catalytic Activity of Zirconium Oxide. *Catal. Lett.* **2014**, *144*, 301–307. [[CrossRef](#)]
210. Alamelu, K.; Raja, V.; Shiamala, L.; Jaffar Ali, B.M. Biphasic TiO₂ nanoparticles decorated graphene nanosheets for visible light driven photocatalytic degradation of organic dyes. *Appl. Surf. Sci.* **2018**, *430*, 145–154. [[CrossRef](#)]
211. Zhang, R.; Ma, Y.; Lan, W.; Sameen, D.E.; Ahmed, S.; Dai, J.; Qin, W.; Li, S.; Liu, Y. Enhanced photocatalytic degradation of organic dyes by ultrasonic-assisted electrospray TiO₂/graphene oxide on polyacrylonitrile/β-cyclodextrin nanofibrous membranes. *Ultrason. Sonochem.* **2021**, *70*, 105343. [[CrossRef](#)]
212. Nguyen, C.H.; Tran, M.L.; Tran, T.T.V.; Juang, R.-S. Enhanced removal of various dyes from aqueous solutions by UV and simulated solar photocatalysis over TiO₂/ZnO/rGO composites. *Sep. Purif. Technol.* **2020**, *232*, 115962. [[CrossRef](#)]
213. Truong, N.T.; Thi, H.P.N.; Ninh, H.D.; Phung, X.T.; Tran, C.V.; Nguyen, T.T.; Pham, T.D.; Dang, T.D.; Chang, S.W.; Rene, E.R.; et al. Facile fabrication of graphene@Fe-Ti binary oxide nanocomposite from ilmenite ore: An effective photocatalyst for dye degradation under visible light irradiation. *J. Water Process. Eng.* **2020**, *37*, 101474. [[CrossRef](#)]
214. Chen, C.; Cai, W.; Long, M.; Zhou, B.; Wu, Y.; Wu, D.; Feng, Y. Synthesis of Visible-Light Responsive Graphene Oxide/TiO₂ Composites with p/n Heterojunction. *ACS Nano* **2010**, *4*, 6425–6432. [[CrossRef](#)] [[PubMed](#)]
215. Xu, T.G.; Zhang, L.W.; Cheng, H.Y.; Zhu, Y.F. Significantly enhanced photocatalytic performance of ZnO via graphene hybridization and the mechanism study. *Appl. Catal. B* **2011**, *101*, 382–387. [[CrossRef](#)]
216. Zhu, M.; Chen, P.; Liu, M. Graphene Oxide Enwrapped Ag/AgX (X = Br, Cl) Nanocomposite as a Highly Efficient Visible-Light Plasmonic Photocatalyst. *ACS Nano* **2011**, *5*, 4529–4536. [[CrossRef](#)] [[PubMed](#)]
217. Ng, Y.H.; Iwase, A.; Kudo, A.; Amal, R. Reducing Graphene Oxide on a Visible-Light BiVO₄ Photocatalyst for an Enhanced Photoelectrochemical Water Splitting. *J. Phys. Chem. Lett.* **2010**, *1*, 2607–2612. [[CrossRef](#)]
218. Zhang, X.Y.; Li, H.P.; Cui, X.L.; Lin, Y.H. Graphene/TiO₂ nanocomposites: Synthesis, characterization and application in hydrogen evolution from water photocatalytic splitting. *J. Mater. Chem.* **2010**, *20*, 2801–2806. [[CrossRef](#)]
219. Zhang, X.; Quan, X.; Chen, S.; Yu, H. Constructing graphene/InNbO₄ composite with excellent adsorptivity and charge separation performance for enhanced visible-light-driven photocatalytic ability. *Appl. Catal. B* **2011**, *105*, 237–242. [[CrossRef](#)]
220. Luciano, A.J.R.; Soletti, L.D.S.; Ferreira, M.E.C.; Cusioli, L.F.; Andrade, M.B.D.; Bergamasco, R.; Yamaguchi, N.U. Manganese ferrite dispersed over graphene sand composite for methylene blue photocatalytic degradation. *J. Environ. Chem. Eng.* **2020**, *8*, 104191. [[CrossRef](#)]
221. Gratzel, M. Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. *J. Photochem. Photobiol. A* **2004**, *164*, 3–14. [[CrossRef](#)]
222. Gao, E.; Wang, W.; Shanga, M.; Xua, J. Synthesis and enhanced photocatalytic performance of graphene-Bi₂WO₆ composite. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2887–2893. [[CrossRef](#)] [[PubMed](#)]
223. Fu, Y.; Chen, Q.; He, M.; Wan, Y.; Sun, X.; Xia, H.; Wang, X. Copper Ferrite-Graphene Hybrid: A Multifunctional Heteroarchitecture for Photocatalysis and Energy Storage. *Ind. Eng. Chem. Res.* **2012**, *51*, 11700–11709. [[CrossRef](#)]